LIBRARY.

The Library is open for reference and for the issue and return of books, daily from 10 A.M. to 6 P.M. (Saturdays 10 A.M. to 1 P.M.); and in the evenings of those days on which the Chemical Society meets.

PUBLICATIONS OF THE SOCIETY.

With the exception of certain numbers of the Journals and Proceedings which are out of print, the following publications may be obtained from Messrs. Gurney and Jackson, 33, Paternoster Row, E.C.4.

	Price to Fellows.			Price to Public.		
	£	s.	d.	£	s.	d.
Memoirs and Proceedings, 1841—1847 (3 Vols.) ... per vol.	1	0	0	1	10	0
Quarterly Journal, 1848—1862 (14 Vols.) ... ... per vol.	1	0	0	1	10	0
,, ,, ,, ,, (Single Parts) .. ... per part		5	0		7	6
Journal, 1862—1895 ... ... per ann.	1	10	0	1	10	0
,, ,, ,, (Single Parts) ... . per part		2	6		2	6
,, 1896—1914 ... ... per ann.	2	0	0	2	0	0
,, ,, (Single Parts) ... ... per part		3	6		3	6
Journal and Proceedings, 1915 (onwards)... ... ... per ann.	3	0	0	3	0	0
,, ,, ,, ,, (Single Parts) per part		5	0		5	0
*Proceedings, 1885—1914 ... ... per vol.		7	6		7	6
,, ,, (Single Parts) ... ... per part			6			6
Annual Reports on the Progress of Chemistry (bound in cloth)						
Vol. I (1904) to present date ... ... per vol.		4	6		4	6
Collective Index, Vol. I. 1841—1872 ... ... per vol.		4	0		4	0
† ,, ,, ,, II. 1873—1882 ... ... per vol		10	0		15	0
† ,, ,, ,, III. 1883—1892 ... ..., per vol.		15	0	1	0	0
† ,, ,, ,, IV. 1893—1902 ... ... per vol.	1	0	0	1	10	0
† ,, ,, ,, V. 1903—1912 ... ... per vol.	2	0	0	2	10	0
‡Jubilee Volume (giving history of the Chemical Society						
from 1841—1891)		2	6		2	6
‡Memorial Lectures, 1893—1900 (out of print)		7	6		7	6
,, ,, Volume II. 1901—1913		6	0		6	0
‡Library Catalogue, 1886		1	0		1	0
‡ ,, ,, 1903		2	6		2	6
‡Cases for binding the Journal in 4 vols. ... ... per ann.		5	0		5	0

Tables of International Atomic Weights for 1918 (as recommended by the International Atomic Weights Committee) :

> ON CARDS : 1s. per dozen ; 4s. for 50 ; 7s. 6d. per 100.
> Postage extra.

> ON PAPER : 4d. per dozen ; 1s. for 50 ; 1s. 9d. per 100.
> Postage extra. (Suitable for pasting into Note Books.)

* Included with Journal as from January, 1915.
† Postage to Fellows One shilling extra.
‡ Post free to Fellows.

The Journal, which is published on the last day of each month, includes the Proceedings and Transactions of the Chemical Society and Abstracts of chemical papers.

The Annual Reports on the Progress of Chemistry contain an epitome of the principal definite steps in advance which have been made during the year. Fellows can obtain from the Assistant Secretary cases for binding the Annual Reports, price One Shilling each.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS.

ERRATA.

Vol. 111 (Trans., 1917.)

Page	Line	
243	15*	*for* "water" *read* "oxygen."

Vol. 112 (Abstr., 1917).

ii 112	7	*for* "nitrate" *read* "nitrite."

Vol. 111 (Abstr., 1918).

ii. 102	$\begin{cases} 15" \\ 14" \end{cases}$	*delete* "[See *Ind.*, 71A]."

Collective Index, 1903–1912.

Authors.

	Col.		
886	i.	22	*for* "*Butea fundosa*" read "*Butea frondosa*."

Subjects.

278	i.	20	*for* "A., ii, 868" *read* "A., i, 868.

Note to T., 1917, 111, 664—665.

The word "pure" in this section is intended to convey that the zinc sulphide in question was free from any intentional impurities and that, so far as could be provided, it was also free from quantities of impurity detectable by ordinary chemical methods. It was not intended to suggest that the sulphide was spectroscopically pure. The methods of preparation described in the section obviously cannot provide against the contamination of the product with traces of zinc oxide.

---

* From bottom.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

INDEX OF AUTHORS' NAMES.

IN TRANSACTIONS AND ABSTRACTS.

Spiegel, L., and H. Szydlowsky, i, 216.
Stark, J., ii, 141.
Stark, J., M. Görcke, and M. Arndt, ii, 141.
Stoll, A. See R. Willstätter.
Sturm, W. See J. Böeseken.
Szydlowsky, H. See L. Spiegel.

T.

Trautz, M., ii, 151.
Trautz, M., and V. P. Dalal, ii, 162.
Travers, A., ii, 176, 177.
Troendle, A., i, 244.
Trunkel, H., ii, 179.

Underwood, J. E. See S. C. Lind.

V.

Vegard, L., ii, 144.
Vegard, L., and H. Schjelderup, ii, 156.
Vournasos, A. C., ii, 168.

W.

Wachenheim, L. See M. Bodenstein.
Wagner, ii, 174.
Wahl, G., i, 236.
Walter, J., ii, 163.
Webster, D. L., ii, 144.
Weiser, H. B., ii, 148.
Weisfelt, (Mlle.) J. See J. Böeseken.
Wenzing, M. See R. Kremann.
Westman, L. E., and R. M. Rowat. i, 246.
White, W. P., ii, 149.
Whittemore, C. F. See S. C. Lind
Willstätter, R., and A. Stoll. i, 243.
Winkler, L. W., ii, 176.
Wolff, J. See B. Geslin.

Z.

Zambonini, F., ii, 170.
Zincke, T., and R. Dereser, i, 220

ERRATA.

COLLECTIVE INDEX, 1903–1912 (SUBJECTS).

Page	Col.	Line	
1317	ii.	23* and 24*	should be deleted.
1326	ii.	30*	below this line *insert* "**3-Methoxy-4-toluic acid,** methyl ester" (GUILLAUMIN), 1910, A., i, 375

* From bottom.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

IX OF AUTHORS' NAMES.

IN TRANSACTIONS AND ABSTRACTS.

ERRATA.

VOL. 114 (ABSTR., 1918).

Page	Line	
i, 282	25	*for* "GALBRANSEN" *read* "GULBRANSEN."
ii, 95	8	" "ZACHS" " "LACHS."

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS.

ERRATUM.

VOL. 114 (ABSTR., 1918).

Page	Line	
i, 275	15	*for* " FRIDRICIA " *read* " FRIDERICA."

CONTENTS.

INDEX OF AUTHORS' NAMES.

IN TRANSACTIONS AND ABSTRACTS.

ERRATA

COLLECTIVE INDEX (AUTHORS'), 1903—1912.

VOL. 111 (TRANS., 1917).

VOL. 113 (TRANS., 1918).

* From bottom.

the courtesy of these authors, to obtain a specimen of the tri-
methyl glucose prepared by them. This specimen, which had been
kept for some months, was found to melt at 114°, but after re-
crystallisation it melted at 117°.   The solubilities, crystalline
form, and melting point of this recrystallised specimen, and also a
mixed melting-point determination (117—118°), proved the identity
of the two specimens, so that there can be no doubt that the colour-
less, crystalline substance obtained as the second cleavage product
of heptamethyl methyllactoside is a trimethyl glucose.

The initial value for the specific rotation in methyl alcohol was
determined, namely, $[a]_D + 112\cdot9°$; after catalysis with a trace of
hydrochloric acid, the reading diminished to an equilibrium value
$[a]_D + 69\cdot1°$. It will be seen that the initial rotation recorded is
slightly higher than the value ($[a]_D + 103\cdot9°$) quoted by Denham
and Woodhouse (loc. cit.), whilst the equilibrium value is almost
identical with that quoted by them for an acetone substance of the
substance (69·5°). This slight variation in the magnitude of the
initial rotation may be explicable on the ground that the melting
point found by ourselves is 8° higher than that quoted by the
former authors in their communication, so that from methylate
lactose the compound may be more readily obtainable as a pure
stereochemical form.   The crystalline compound combines with
phenylhydrazine in the cold, giving an oily phenylhydrazone, but
no phenylosazone derivative could be prepared.

We can also confirm the constitution assigned to this compound,
and a discussion of the formula (VI) is included in the theoretical
part of this communication.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
         UNIVERSITY OF ST. ANDREWS.

Recent Studies on Active Nitrogen.

A Lecture delivered before the Chemical Society on
February 21st, 1918.

By the Hon. ROBERT JOHN STRUTT.

IN 1913 I gave a Friday evening lecture at the Royal Institution,
in which some of the more striking phenomena of active nitrogen
were exhibited. This evening I shall dwell chiefly on results
obtained since that time, but to be intelligible to those coming
fresh to the subject, it will be necessary to traverse a little of the
old ground.

The fundamental experiment on this subject is to pass a stream
of rarefied nitrogen through a discharge tube a (Fig. 1) in which
a vigorous jar discharge is maintained. The stream of gas, drawn
by a powerful air pump, issues into the vessel b, where it exhibits
a brilliant yellow light. The fact that no electric discharge passes
in b and that the gas takes an appreciable time to pass through
this vessel shows that it remains glowing after the electric dis-
charge is over, and this may be established very directly by simply
turning the exciting discharge off, when the luminosity will be
seen to persist for some seconds' interval flowing down into the
pump. Indeed, in favourable circumstances and with a closed
vessel scrupulously clean, the luminosity persists for several
minutes.

Evidently this luminosity (which is not of the nature of
temperature-radiation) can only be maintained by the passage of
the nitrogen gas from a state in which it contains more potential
energy to a state in which it contains less. This circumstance alone
might suggest that a special modification of nitrogen is present,
but this becomes a certainty when we note the behaviour of the
glowing gas when other gaseous substances are brought in contact
with it. For it is found that hydrocarbons are converted at the
ordinary temperature into hydrocyanic acid, and that the more
volatile metallic vapours are converted into nitrides.

Ordinary nitrogen will certainly not behave in this way, and
therefore it does not seem over-bold to assume that an extraordinary
kind of nitrogen is present. This has been named, with a mini-
mum of hypothesis, active nitrogen. So far as I am aware, no
alternative interpretation of the facts mentioned has been
attempted.

In some of the developments of radioactivity, it has been an
unfortunate necessity to work with quantities so small that often

they could not be weighed or even seen. It may be remarked in passing that whatever legitimate scepticism may have been felt about results so attained, at any rate they have led to conclusions which can be verified by the well-tried methods of the chemical analyst. It suffices to refer to the now established fact that there are various kinds of lead of different atomic weights.

There is, or has been, an idea abroad that my conclusions on active nitrogen are dependent on similar indirect methods: that the evidence for the existence of an active modification of nitrogen depends on a dubious interpretation of obscure spectroscopic phenomena. I hope this evening to make it quite clear that this is not the case. In fact, I should not have had the courage to face you to-night if I had not had more direct and convincing evidence to offer. I wish to emphasise that the existence of active nitrogen was formulated solely on the grounds which appeal most directly

FIG 1.
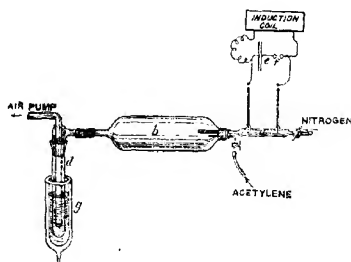
to chemists. The properties of this substance have been examined by the ordinary methods of chemical analysis, carried out in many cases, not on a microscopic scale, but in vessels of ordinary or even large size, dense precipitates and strong colorations being obtained such as do not require the eye of faith for their recognition.

Although the luminous phenomena accompanying these actions form no part of the evidence for the existence of the active substance, yet they are of considerable interest in connexion with its properties, and I shall have a good deal to say about them.

I first show you the action of active nitrogen on acetylene. When acetylene enters the stream of yellow, glowing gas, you see that a lilac tint is developed. This shows the well-known cyanogen spectrum—the spectrum obtained, for instance, from burning cyanogen; and it was for this reason that it was first suspected that hydrocyanic acid was formed. It would, however, be most

K 2

unsatisfactory to rely on such an argument. I do not, and never did rely on it. In showing the presence of hydrocyanic acid, I have generally frozen it out from the gas stream with liquid air (as in Fig. 1) and shown its presence chemically in the cooled vessel *d*. To-night, however, a simpler method must suffice. We lead the gas ejected by the pump through a solution of sodium hydroxide to collect the hydrocyanic acid. On adding a mixture of ferrous and ferric salts, and acidifying, you see that a strong Prussian-blue reaction is obtained.

I have shown on previous occasions the action of active nitrogen on mercury vapour. Mercury was gently heated in a stream of the yellow, glowing gas, and it was found that the yellow glow was displaced by the green light of mercury, familiar in the mercury vapour lamp, with its characteristic line spectrum. At the same time, a nitride is produced. This may be treated with water, when

FIG. 2.
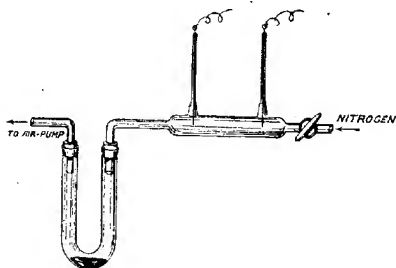
ammonia is formed, and the Nessler reaction is obtained. The nitride is unstable, and when heated pretty strongly it decomposes with minute flashes, accompanied by audible crackling.

I shall now perform a novel experiment, not before shown publicly. This is the action of active nitrogen on cold liquid mercury. The stream of glowing gas is led over a U-tube (Fig. 2) containing a small quantity of clean mercury, not enough to fill the bottom bend of the tube. So long as the tube is at rest nothing happens, the glowing gas passing on; but if the tube is shaken so as to break the skin of the mercury surface, and constantly to renew it, it is seen that the mercury is quickly attacked and becomes foul, very much after the fashion in which it is made foul by ozone. At the same time, the luminosity of the issuing gas is extinguished, showing that it is no longer in the peculiar state.

Let us now take some of the mercury which has been made foul

in this way, mix it with water, distil off a portion, and test with Nessler's solution.   You will have no difficulty in recognising the presence of ammonia, showing that a nitride had been formed.

One interesting point is that when liquid mercury is employed in this way we do not get any trace of the mercury spectrum, so conspicuous when active nitrogen mingles with mercury vapour, but the chemical reaction occurs none the less.   Thus it appears that we cannot trace any close or necessary connexion between the luminous effects and the chemical ones.

I will now direct your attention to another interesting case of this kind.   Suppose that nitrogen is purified by allowing it to remain over cold phosphorus, and then thoroughly dried by passage through long and tightly packed tubes filled with phosphoric oxide. In these circumstances, it will be tolerably free from traces of oxygen compounds, and the afterglow of the gas, usually yellow, will be found to be practically invisible through a blue glass. Suppose now that we allow a small quantity of almost any oxygen-containing gas to flow into the stream of glowing nitrogen, taking care, however, to prevent it from mixing with the nitrogen until the latter has left the discharge.   Nothing particular seems to happen when the oxygen compound flows in, so long as we observe the yellow light directly, except that the yellow light fades out sooner; but if a blue glass is interposed to cut out the yellow light, then we see that at the confluence a bluish-violet light is developed by admixture of the gases.   This bluish-violet light is to a great extent masked by the yellow when no colour-filter is used.

The same thing can be recorded photographically, using first an isochromatic plate with yellow screen, then an ordinary plate with a blue screen.*

Oxygen itself, or carbon monoxide or dioxide, or nitrous or nitric oxides, will give this effect when introduced into the yellow-glowing gas.   I wish you particularly to notice that in these experiments the admixture does not get back to the discharge tube.   It never comes in contact with the electric discharge at all.   Only nitrogen goes through the discharge.   The oxygen-containing gas is mixed with it afterwards.

The yellow light when spectroscopically analysed shows a selection of the bands produced by nitrogen in a vacuum discharge, although omitting many of them in a very strange way.   It is simply a nitrogen spectrum.   But what of the bluish-violet light? Although I have spoken of it as bluish-violet, it is really in the main ultra-violet, and it consists of two sets of bands, which have

---

* Or no screen at all, for the photographic action of the yellow light in the latter case is relatively too weak to be worth considering.

been called, for the sake of distinction, the β- and γ-groups of bands. The β-bands are not at present known to be produced in any other way, but the γ-bands occur when oxides of nitrogen (nitrous or nitric) are introduced into a Bunsen flame. They do not occur in a Bunsen flame burning in the ordinary way, which, of course, contains oxygen and nitrogen separately, and these facts, taken together, would seem to suggest very distinctly that the spectrum in question indicates oxidation of nitrogen. Is there, then, any oxidation when oxygen is led into active nitrogen, and this spectrum results? Careful tests of the products with the extremely sensitive tests available (Griess's reagent) have convinced me that no oxides of nitrogen are produced. I have been reluctant to accept this conclusion, and have returned again and again to the subject, always with the same result. It would have been satisfactory to find that the isolation of active nitrogen would help us to understand the processes occurring in the arc process for oxidising nitrogen, and it is still possible that something of the kind may be made out. Koenig and Elöd in Germany have stated that a particular kind of active oxygen (not ozone) can be produced by electric discharge which will unite directly with active nitrogen. I have attempted to repeat these experiments, but have hitherto been unable to satisfy myself of their correctness. I do not wish, however, to speak too positively on the subject.

However this may be, it is remarkable that whilst active nitrogen will attack carbon compounds, even methane, to form hydrocyanic acid, it will not react either with oxygen or with hydrogen.

Hitherto, we have considered chiefly the properties of active nitrogen when formed. It is also of interest to consider the conditions for its formation. These present many puzzling problems, and in this connexion I shall have to content myself chiefly with recording facts rather than theories.

Let us first consider what kind of electrical conditions are best. In the first place, it is far preferable to work at a low gaseous pressure, a few mm. of mercury. The reason for this seems to be that collision with ordinary nitrogen molecules tends in some way to the destruction of active nitrogen, although how this occurs is not clear.

The next point is that a Leyden jar discharge is much preferable to the discharge of an induction coil without a jar. As is well known, the effect of the jar is to store up electricity and allow it to discharge suddenly through the gas. In these circumstances, the momentary current density is very high, and the nature of the discharge is altered in other respects: the peculiar phenomena of negative dark space and negative glow are obliterated, and the

spectrum of the light along the length of the discharge is modified, losing its reddish colour and becoming much bluer. At the same time, the production of active nitrogen is much increased. Accordingly, the jar discharge is generally used in experiments on active nitrogen.

Not only is the jar discharge the best, but if an uncondensed discharge (without jar) passes through the gas after a jar discharge, it is positively destructive, undoing part of the work which has been done by the jar discharge. This is illustrated by the experiment of Fig. 3. We allow a stream of the rarefied nitrogen to pass in succession through the discharge tubes A and B and the observation vessel C. The jar discharge passing in A produces active nitrogen, recognised by the orange glow. If we start an uncondensed discharge in B, leaving other conditions unchanged, the

FIG. 3.
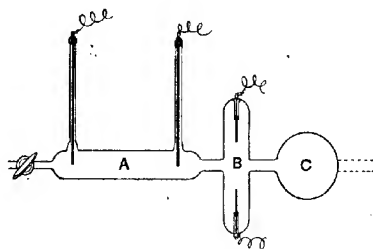
brilliancy of the glow in C is diminished, proving the destructive effect above referred to.

This and other evidence proves that the production of active nitrogen by the discharge is of the nature of a reversible reaction. The concentration only attains a certain limit, which may be lowered if the conditions become less favourable.

We may consider the analogy of this to better known cases of the production of endothermic substances. Consider, for instance, the known production of ozone from oxygen by the action of a high temperature. The concentration of ozone increases with the temperature of the hot tube, and the object is to cool the hot gases as quickly as possible, so as to preserve the concentration characteristic of a high temperature. If we subsequently passed the ozonised oxygen through a less strongly heated tube, we should find the concentration lowered thereby. In directing attention to this analogy, I do not wish to commit myself to the view that the action of the discharge is necessarily due to high temperature. There

are many doubts and obscurities overshadowing any theory of that kind.

Although, as we have seen, the condensed discharge is the most efficient for activation of nitrogen, it is worth while to go back for a moment to the uncondensed discharge, or steady current through

FIG. 4.

the gas, produced preferably by means of a high-tension continuous-current dynamo. In this case, the discharge presents several distinct features. There is the Crookes's dark space near the cathode, the blue negative glow, gradually fading off to the darkness of the Faraday dark space, and then the red, positive column extending to the anode. These features are indicated in the slide (Fig. 4). We may draw a current of nitrogen transversely across any part of this discharge (the apparatus used is shown in Fig. 5) and obtain activation. As might be expected, the intensity of activation is not the same in the different parts of the discharge. The ordinates of the curve drawn above the figure of the discharge tube show the comparative intensities in the different parts of the tube, and it will be seen that the blue negative glow, particularly in the immediate neighbourhood of the cathode, is the part of the discharge where activation is strongest. It is worth noticing, and may be significant, that the bluer kind of discharge, whether obtained by approaching the cathode or by introducing a Leyden jar, is the more efficient in producing active nitrogen.
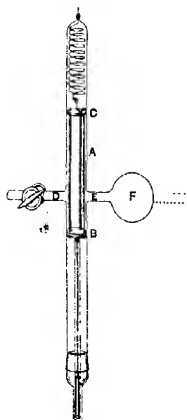
FIG. 5.

Much more might be said about the electrical conditions for producing active nitrogen, but I will pass to what, from the chemical point of view, may be of more interest. In the Royal Institution lecture in 1913, which has been mentioned, I referred to certain conclusions which Comte, and also Tiede and Domcke,

had reached in Germany. Their conclusion was that the pheno
mena which I had described in connexion with active nitrogen did
not occur unless the gas contained traces of oxygen, and the last
two authors went so far as to conclude from this that there was
no such thing as active nitrogen. I said at the time that I was
satisfied they were entirely mistaken as to the necessity for oxygen;
but I now recognise that I spoke over confidently, and that this
was too strong an expression to use. I think you will agree with
me that the experiments I have shown you this evening on the
formation of hydrocyanic acid and of nitrides are not easy of
interpretation if the existence of active nitrogen is denied; but
there was this much of truth in Tiede and Domcke's conclusion—
that very pure nitrogen does not yield active nitrogen under the
influence of the discharge, and that a trace of oxygen added will
make it do so. What they did not discover, but what I have found
since, is that a trace of almost any admixture will have the same
effect. For instance, a trace of methane or ethylene will do it, or,
again, carbon dioxide, or carbon monoxide, or hydrogen sulphide,
or mercury vapour. In the experiments on which I relied when
I denied the validity of Tiede and Domcke's work, my attention
was concentrated on the removal of any trace of free oxygen; this
did not result in reducing the glow, and I now appreciate that this
was because other impurities were present. I was right in denying
that oxygen was essential, but I was wrong in saying that pure
nitrogen was all that was needed.

The method which I have generally used for preparing nitrogen
is to take the commercial compressed gas, prepared by the rectifica-·
tion of liquid air, and to store it over water in a gas holder, in
which is hung up a perforated metal bucket containing phos-
phorus. Gas prepared in this way always gives active nitrogen
freely. To begin with, it is moist. I have always dried it with
an ordinary tube of phosphoric oxide, but if the spectrum of the
glow is photographed, it still shows the β- and γ-groups of bands
characteristic of oxygen compounds present in active nitrogen.
Passage over very long tubes tightly packed with granular phos-
phoric oxide reduces the intensity of these bands almost to the
vanishing point.

When they disappear, however, another impurity is unmasked,
for the violet and ultra-violet bands characteristic of cyanogen
compounds appear, showing that hydrocarbons are present, and
react with the active nitrogen to yield this spectrum. I have
tried to get rid of these cyanogen bands by employing specially
pure phosphorus, which I owe to the kindness of Mr. Albright, but
without success. We cannot get pure nitrogen by this method,

K*

although it is fairly successful in removing oxygen and oxygen compounds.

I have not hit on any really convenient plan for getting nitrogen so free from impurities that it does not yield active nitrogen. The method that has served me best is to heat the commercial gas in a globe of 4 litres capacity for many hours at 300° with metallic sodium. It is desirable, if not absolutely necessary, to avoid using sodium which has been stored in oil, and thus contaminated with hydrocarbons. The globe once set up serves for repeated charges of nitrogen, and seems to perform better after it has been used repeatedly.

Hot sodium has the advantage of destroying nearly all the impurities that might be present in the nitrogen, for example, oxygen, water vapour, carbon dioxide, hydrocarbons. Hydrogen, it is true, is apt to be liberated, but this for the present purpose is comparatively unimportant. Gas taken from the globe A (Fig. 6) (which is allowed to cool after the purifying process is

FIG. 6.
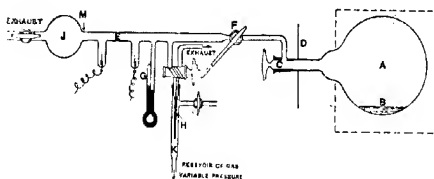
over) is led through the discharge tube E and the bulb J, when, if any active nitrogen is produced, we shall see the characteristic glow. The glow from the gas purified in this way may be got very faint, verging on invisibility, and we can then restore it by admission of a suitable impurity in very minute amount through the capillary tube H. The exact manipulation in connexion with this admission of the gas need not detain us now; I have described it in one of my Royal Society papers. The general method is to increase the feed at the outer end of the capillary from low pressure towards atmospheric pressure until the effect becomes appreciable.

The flow of nitrogen was regulated by hand, so as to maintain a rate of 2·6 litres per hour, and the tributary stream through the fine capillary could be compared with this, so as to show what fraction of impurity was being added. With oxygen, for instance, the effect was perceptible with a tributary stream of 1 c.c. per hour, and 3·5 c.c. produced the maximum effect. In the latter case, the oxygen added was 1/750th part of the whole. If we add

much more oxygen than this, the yellow glow begins to be spoilt, and 2 per cent. admixture destroys it altogether.

As I have explained, oxygen is not the only admixture that brings in the yellow glow again. Among gases that do not contain oxygen, hydrogen sulphide, ethylene, and methane will do the same. Methane acted when present in very small concentrations. It had a perceptible effect when only 1/30,000th part was added to the nitrogen stream.

I have seen a criticism of these experiments in which it is suggested that no sufficient precautions were taken to guard against traces of oxygen or oxygen compounds in these added gases. This criticism does not seem to be well considered. If, for instance, we supposed the "methane" (which, as a matter of fact, was carefully prepared from aluminium carbide and purified by liquefaction and fractional evaporation) to *consist entirely of pure oxygen*, the observed facts would not be covered, for the methane added in the experiment just cited was only about 1/10th of the minimum amount of oxygen required to produce an observable effect.

This action of foreign substances in encouraging the production of active nitrogen is very mysterious, although not perhaps more so than the necessity for minute traces of water in many commonplace chemical reactions, which has been so admirably established by my colleague, Prof. Baker. I was at one time hopeful of connecting it with a change in the conditions of the electric discharge, and it is true that the introduction of a trace of oxygen, for example, considerably increases the drop of potential over the cathode at the same time that it increases the yield of active nitrogen. On the other hand, we may arrange so that the stream of nitrogen gas does not reach the cathode, but is led away after being exposed to the positive part of the discharge only. In this case, we find that a trace of oxygen produces the usual favourable effect on the generation of active nitrogen without at all affecting the electrical conditions in that part of the discharge which is operative.

The whole of this part of the subject requires further study; and, in conclusion, I must admit that investigations, now lasting more than seven years, have only touched the fringe of the subject.

XXIV.—*Studies in the Phenylsuccinic Acid Series. Part VI. Racemisation Phenomena Observed during the Investigation of the Optically Active Phenyl- and Diphenyl-succinic Acids and their Derivatives.*

By HENRY WREN.

IT has been recently shown (Wren and Still, T., 1917, **111**, 1019) that the esters of *r*- and *meso*-diphenylsuccinic acids are interconvertible under the influence of alkali. To quote a specific example, ethyl *r*-diphenylsuccinate is almost quantitatively transformed into the ester of the *meso*-acid when its alcoholic solution is treated with a solution of sodium ethoxide in ethyl alcohol; also, when the ester is hydrolysed with an insufficient amount of aqueous ethyl-alcoholic potassium hydroxide solution, the non-hydrolysed portion is found to have suffered partial isomerisation, with the production of ethyl *meso*diphenylsuccinate. Since, in solution at any rate, ethyl *r*-diphenylsuccinate may be regarded as a molecular mixture of ethyl *d*-diphenylsuccinate and ethyl *l*-diphenylsuccinate, it was to be expected that the esters of the optically active acids would separately undergo similar transformation, and would therefore become racemised, the possibility of a balanced action being excluded in this case, since any further isomerisation of the *meso*-ester which might be formed would merely lead to the production of the *r*-ester. The theoretical expectations have been fully confirmed by a series of experiments with the methyl and ethyl esters of the optically active acids. A typical example is furnished by the formation of ethyl *meso*-diphenylsuccinate as a product of the action of ethyl-alcoholic sodium ethoxide on ethyl *l*-diphenylsuccinate. Similarly, when ethyl *d*-diphenylsuccinate is hydrolysed with an insufficient amount of aqueous ethyl-alcoholic potassium hydroxide solution, the non-hydrolysed portion is found to be almost inactive towards polarised light and to consist practically entirely of ethyl *meso*diphenylsuccinate. It would thus appear that the racemisation previously observed to occur during the hydrolysis of esters of the optically active diphenylsuccinic acids (Wren and Still, T., 1915, **107**, 1454) takes place in part, at any rate, previous to the actual hydrolysis, and is thus due to rearrangement of the ester, and not of the acid. The greater liability of esters as compared with the corresponding acids to racemisation under the influence of alcoholic alkali has been pointed out by Gadamer (*Chem. Zeit.*, 1910, **34**, 1004; *J. pr.*

Chem., 1913, [ii], **87**, 312), who found that, whilst the esters of tropic acid are readily racemised, the acid itself is not racemised by hydroxyl ions. This difference in behaviour is ascribed to the ionisation of the acid at the carboxyl group, whilst the ester, which behaves as a pseudo-acid, only becomes ionised in the presence of hydroxyl ions, thus:

$$\underset{\text{Tropic acid.}}{\overset{C_6H_5}{\underset{HO \cdot CH_2}{>}}C<\overset{H}{\underset{CO_2H}{}}} \qquad \underset{\text{Esters of tropic acid.}}{\overset{C_6H_5}{\underset{HO \cdot CH_2}{>}}C<\overset{H}{\underset{CO_2R}{}}}$$

$$\downarrow \qquad\qquad\qquad\qquad \downarrow$$

$$\overset{C_6H_5}{\underset{HO \cdot CH_2}{>}}C<\overset{H}{\underset{CO_2}{}} \qquad \overset{C_6H_5}{\underset{HO \cdot CH_2}{>}}C<_{CO_2R}$$
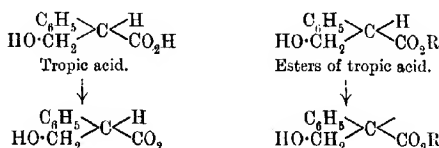
It has, however, been pointed out by Frankland (T., 1913, **103**, 725) that the racemisation may be due to loss of asymmetry caused by tautomeric change previous to ionisation, thus:

$$\overset{C_6H_5}{\underset{HO \cdot CH_2}{>}}C<\overset{H}{\underset{CO_2R}{}} \quad \longrightarrow \quad \overset{C_6H_5}{\underset{HO \cdot CH_2}{>}}C:C<\overset{OH}{\underset{OR}{}}$$
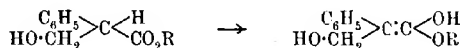
The only instance of racemisation of an ester previous to hydrolysis which appears to have been noted in the literature is the observation of McKenzie and Widdows (T., 1915, **107**, 713) that *l*-menthyl *d*-phenyl-*p*-tolylacetate is, in part, catalytically racemised by alkali prior to its undergoing hydrolysis. In a case which presents some analogies, Wren (T., 1909, **95**, 1596) found that the portion of the ester which escapes conversion into amide is partly inactivated when methyl *l*-mandelate is acted on by cold alcoholic ammonia.

The observations have been extended to the optically active phenylsuccinic acids and their esters, since the latter substances are much more readily soluble than the derivatives of the diphenyl-succinic acids, and therefore allow the course of racemisation to be followed directly by polarimetric measurement. It is thus found that ethyl and methyl *d*-phenylsuccinates are rapidly and completely racemised by the action of a solution of the requisite sodium alkyloxide in the corresponding alcohol, and also that when the latter ester is treated with potassium hydroxide dissolved in slightly aqueous ethyl alcohol in quantity insufficient for complete hydrolysis, the non-hydrolysed portion is almost completely racemised under the conditions described in the experimental section of the paper.

Some time ago, it was found by Wren and Williams (T., 1916, **109**, 579) that a partly racemised acid was obtained when methyl *d*-phenylsuccinate is hydrolysed by an excess of aqueous ethyl-

alcoholic potassium hydroxide solution. Thus, in one experiment, the ester was heated with about six times the theoretically necessary quantity of potassium hydroxide dissolved in aqueous ethyl alcohol (water:alcohol::1 vol.:2 vols.), when the recovered acid was found to have $[\alpha]_D + 110.2°$ in acetone solution, whilst the parent acid had $[\alpha]_5^{12.5} + 175.4°$. The considerable activity of this acid became somewhat remarkable when considered in conjunction with the almost complete racemisation of the non-hydrolysed ester in the experiment just quoted, and pointed to a profound influence of the varying factors, namely, the amount of potassium hydroxide and the water content of the solution. The effect of variation in the latter was therefore studied, and was found to exercise a very marked influence on the optical activity of the recovered acid. In three strictly comparable experiments, in which the only differences consisted in the use of absolute, approximately 80 per cent. and 50 per cent. alcohol respectively, the acid formed by hydrolysis was found to have $[\alpha]_D + 3.1°$, $+59.1°$, and $+100.3°$ respectively in ethyl-alcoholic solution in which the parent acid had $[\alpha]_D' + 147.4°$; under closely similar conditions, the latter acid was found to be unaffected by the action of an excess of alcoholic or aqueous-alcoholic sodium hydroxide solution.

During the last few years, a considerable amount of evidence has been accumulated which indicates that racemisation under the influence of alkali may frequently be attributed to keto-enolic desmotropy, with consequent disappearance of the asymmetry of the compound. In the present instance, the inactivation of methyl d-phenylsuccinate when acted on by sodium methoxide may be due to the formation of the enolic form, thus:

$$
\begin{array}{ccccc}
\text{CH}_2\cdot\text{CO}_2\text{Me} & & \text{CH}_2\cdot\text{CO}_2\text{Me} & & \text{CH}_2\cdot\text{CO}_2\text{Me} \\
| & \rightarrow & | & \rightleftarrows & | \\
\text{CHPh}\cdot\text{CO}_2\text{Me} & & \text{CPh} & & \text{CHPh}\cdot\text{CO}_2\text{Me} \\
& & \overset{\parallel}{\text{C}}\!\!<\!\!\begin{array}{l}\text{ONa}\\\text{OMe}\end{array} & &
\end{array}
$$

Active.   Inactive.   Inactive.
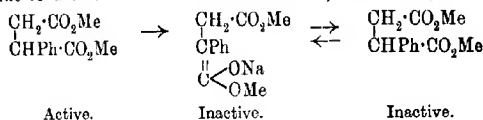
The evidence which has been brought forward in favour of such an explanation of racemisation in analogous case is, so far, of a purely qualitative nature; in no single instance has the enolic form been isolated or its amount determined. The actual separation of the enolic modification would doubtless be a matter of great difficulty in many cases, since the proportion of enolised molecules need be but infinitesimal to account for the phenomena of racemisation. On the other hand, it was hoped to be able to bring quantitative evidence of the presence of the enolic modification by utilising the method adopted by K. H. Meyer (*Ber.*, 1912, **45**, 2864) in his investigations on ethyl malonate and ethyl

methanetricarboxylate. Direct titration of a methyl-alcoholic solution of methyl d- or r-phenylsuccinate with bromine failed to disclose the presence of any enol, and a similar result was obtained when experiments were performed on the esters dissolved in methyl-alcoholic sodium methoxide solution, although under the latter conditions ethyl malonate was found to be largely enolised. The experimental conditions were not greatly varied in this case, however, since the objection could possibly be raised that, in order to demonstrate the point at issue, it would be necessary to show definitely that enolisation occurs in such a manner as to form compound I, and not II :

$$
\begin{array}{ll}
\mathrm{CH_2 \cdot CO_2 Me} & \mathrm{C{<}^{OMe}_{ONa}} \\
\mathrm{|} & \mathrm{||} \\
\mathrm{CPh} & \mathrm{CH} \\
\mathrm{||} & \mathrm{|} \\
\mathrm{C{<}^{ONa}_{OMe}} & \mathrm{CHPh \cdot CO_2 Me} \\
\text{(I.)} & \text{(II.)}
\end{array}
$$
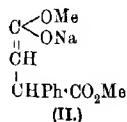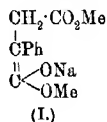
It is hoped to apply the method, however, to esters of certain monobasic acids to which this objection cannot be urged.

Lastly, if racemisation be attributable to the formation of an enolic derivative, it would be expected that the nature of the basic atom or group of the alkali would have an influence on the result. Experiments on the hydrolysis of methyl d-phenylsuccinate with aqueous ethyl-alcoholic tetramethylammonium hydroxide solution were therefore performed ; racemisation was found to be even more pronounced than with potassium hydroxide solution under nearly similar conditions.

EXPERIMENTAL.

Formation of Ethyl meso*Diphenylsuccinate from Ethyl*
d- *and* l-*Diphenylsuccinates.*

A. *By the Action of Ethyl-alcoholic Sodium Ethoxide Solution.*—Ethyl l-diphenylsuccinate (1 gram) was warmed with a solution of sodium ethoxide in ethyl alcohol ($0.666N$; 20 c.c.) in a closed vessel to about 50°, when it dissolved completely; the solution was allowed to cool to the ordinary temperature, when it became almost solid. After remaining during three days at the temperature of the laboratory, the precipitate was removed and washed successively with alcohol, warm water, and, finally, alcohol. It melted at 139—140°, and was optically inactive in acetone solution. After being crystallised from rectified spirit, ethyl *meso*diphenylsuccinate was obtained in well-defined needles melting at 140—141°.

B. *By Partial Hydrolysis.*—Ethyl d-diphenylsuccinate (1·5

grams) was heated during four hours with aqueous ethyl-alcoholic potassium hydroxide solution ($0.25N$; 15 c.c.), this being about three-fifths of the quantity required for complete hydrolysis. The solution was diluted with water, and the unattacked esters were extracted with chloroform. The residue, obtained after removal of the latter, melted at 138—140°; it had $[a]_D + 5.4°$ in acetone solution ($l=2$, $c=1.113$, $a_D + 0.12°$), whereas the pure d-ester has $[a]_D^{16} + 279.4°$ under similar conditions. After being crystallised from rectified spirit, it yielded pure ethyl $meso$diphenylsuccinate, which was optically inactive in acetone solution and melted at 140—141°.

Formation of Methyl mesoDiphenylsuccinate from Methyl l- and d-Diphenylsuccinates.

A. *By the Action of a Methyl-alcoholic Solution of Sodium Methoxide.*—Methyl l-diphenylsuccinate (1 gram) was heated in a stoppered flask during four hours at 55—65° with a solution of sodium methoxide in absolute methyl alcohol ($0.704N$; 60 c.c.). When the solution was cooled, a quantity of fine, prismatic crystals separated, which were removed, washed with water and methyl alcohol, and dried. After being crystallised from acetone, the product was obtained in well-defined needles, which were optically inactive when dissolved in chloroform ($l=2$, $c=0.5115$), and were identified as methyl $meso$diphenylsuccinate by their crystalline form, melting point (218.5—219.5°) alone, and when mixed with an approximately equal quantity of the synthetic $meso$-ester.

B. *By Partial Hydrolysis.*—A solution of methyl l-diphenylsuccinate (1.5 grams) in boiling methyl alcohol (100 c.c.) was heated during four hours with aqueous methyl-alcoholic potassium hydroxide solution ($0.593N$; 8 c.c.), this being approximately half the quantity of alkali required for the complete hydrolysis of this amount of the ester. The alcohol was removed on the water-bath and the residue warmed with water. The undissolved portion was removed and dried. It was optically inactive when dissolved in chloroform ($l=2$, $c=0.8365$), and, after being crystallised from acetone, yielded methyl $meso$diphenylsuccinate, which melted at 218.5—219.5°; the melting point was unaltered by admixture with the synthetic $meso$-ester.

Racemisation of Methyl and Ethyl d-*Phenylsuccinates under the Influence of Alkali.*

A. *By Sodium Alkyloxide.*—Methyl d-phenylsuccinate ($0\cdot8157$ gram) was dissolved in methyl-alcoholic sodium methoxide solution ($20\cdot5$ c.c.), and transferred as rapidly as possible to a 2-dcm. tube. Approximately three minutes after being prepared, the solution had $a_D + 8°$, but the field was somewhat cloudy, and the activity altered too rapidly to allow of accurate measurement. After about fifteen minutes, the value had decreased to $+3\cdot5°$, after forty minutes to $+0\cdot5°$, after seventy minutes to $+0\cdot17°$, after one hundred minutes to $+0\cdot05°$. After two hours, the solution was poured into a slight excess of dilute hydrochloric acid. The ester was extracted with ether, the ethereal solution washed with sodium carbonate, and dried over calcium chloride. The residue, obtained after removal of the solvent, solidified readily, and was optically inactive in acetone solution ($l = 2$, $c = 1\cdot555$). After being crystallised from light petroleum, it yielded characteristic clusters of prisms of methyl r-phenylsuccinate, which melted at $57\cdot5$—$58\cdot5°$. The melting point remained unchanged when the substance was mixed with the synthetic r-ester.

In a similar manner, ethyl d-phenylsuccinate ($0\cdot9964$ gram) was dissolved in ethyl-alcoholic sodium ethoxide solution ($1\cdot069N$; 20 c.c.). In this case, racemisation proceeded so rapidly as to be almost complete before polarimetric measurements could be made, and the solution had become quite inactive within ten minutes. Since the liquid nature of the ethyl r-ester rendered the identification of a small quantity of it a matter of difficulty, water was added to the solution, and the ester hydrolysed. The resulting r-phenylsuccinic acid melted at 167—$168°$, whereas Higson and Thorpe (T., 1906, **89**, 1470) give $168°$ as the melting point of this acid.

B. *By Partial Hydrolysis.*—Methyl d-phenylsuccinate (3 grams) was heated to boiling during two and a-half hours with slightly aqueous methyl-alcoholic potassium hydroxide solution ($0\cdot395N$; 25 c.c.), this being rather more than one-third of the quantity theoretically necessary for complete hydrolysis. The alcohol was removed on the water-bath, and the residue mixed with water and shaken with ether. The residue (about $0\cdot3$ gram) obtained after removal of the ether solidified readily, and had $[a]_D + 2\cdot12°$ when dissolved in acetone ($l = 2$, $c = 1\cdot178$, $a_D + 0\cdot05°$), whereas the pure ester has $[a]_D^{10} + 152\cdot2°$ under similar conditions. After being crystallised from light petroleum (b. p. 40—$60°$), it yielded pure

methyl r-phenylsuccinate, which melted at 57—58·5°; this value remained unchanged after admixture with the synthetic ester.

Action of Alkali on l-Phenylsuccinic Acid.

The l-phenylsuccinic acid used in these experiments had $[a]_D -148·3°$ in ethyl-alcoholic solution, a value which agrees well with the data of Wren and Williams (loc. cit.).

Three comparative experiments were performed, in which the acid (1 gram) was treated in a closed vessel with (a) sodium ethoxide solution (1·059N; 50 c.c.) and absolute ethyl alcohol (20 c.c.); (b) sodium ethoxide solution (50 c.c.), alcohol (20 o.c.), and water (0·95 c.c.), and (c) sodium ethoxide solution (50 c.c.), alcohol (10 c.c.), and water (10 c.c.).   In each case a certain amount of precipitate separated. The mixtures were heated with frequent agitation during five hours at 70°, then neutralised with hydrochloric acid, and evaporated to remove alcohol; the acids were isolated by extraction of the acidified solutions with ether. The dried acids were polarimetrically examined in ethyl-alcoholic solution, the values for the specific rotations being (a) $-146·6°$ ($l=2$, $c=2·8815$, $a_D -8·45°$), (b) $-145·5°$ ($l=2$, $c=1·691$, $a_D -4·92°$), and (c) $-146·2°$ ($l=2$, $c=1·7035$, $a_D -4·98°$). In no case, therefore, was any evidence of racemisation obtained.

Complete Hydrolysis of Methyl d-Phenylsuccinate by Alcoholic Sodium Hydroxide containing differing Proportions of Water.

In these experiments, the weight of ester and alkali, the total volume of the solution, the temperature, and duration were maintained uniform, the only variation consisting in the replacement of differing volumes of alcohol by water. Stock solutions of ester were prepared by dissolving 2 grams of the latter in 30 c.c. of ethyl alcohol, and of alkali by dissolving sodium in absolute ethyl alcohol; the latter solution was 1·1N. Ten c.c. of the ester solution were mixed with (a) alkali solution (25 c.c.), alcohol (25 c.c.), and water (0·45 c.c.); (b) alkali solution (25 c.c.), alcohol (15 c.c.), water (10 c.c.), and (c) alkali solution (25 c.c.), water (25 c.c.). The solutions were heated in closed flasks during four hours at 60—65°; precipitates speedily separated in (a) and (b) but (c) remained homogeneous throughout. The resulting mixtures were nearly neutralised with hydrochloric acid and evaporated to remove alcohol; the aqueous solutions were extracted with ether after acidification with mineral acid. The residual phenylsuccinic acids were polarimetrically examined in ethyl-alcoholic solution, when

the following values were observed for the specific rotation:
(a) $+3.1°$ $(l=2, \quad c=2.2391, \quad \alpha_D +0.14°)$; (b) $+59.1°$ $(l=2,$
$c=1.913, \quad \alpha_D +2.26°)$; (c) $+100.3°$ $(l=2, \quad c=2.0731, \quad \alpha_D +4.16°)$.

Complete Hydrolysis of Methyl d-Phenylsuccinate by Aqueous-Alcoholic Tetramethylammonium Hydroxide Solution.

The solution of the alkali was prepared by warming an aqueous solution of tetramethylammonium iodide with a slight excess of silver oxide, and removal of silver iodide and unchanged oxide. The filtrate was concentrated to 14 c.c., and then diluted with ethyl alcohol to 55 c.c. An approximately N-solution was thus obtained.

The methyl d-ester (1 gram) was heated during two and a-half hours with the solution described above, and the corresponding acid isolated in the usual manner; it melted at 164—168.5°, and had $[\alpha]_D +10.1°$ in ethyl-alcoholic solution $(l=2, \quad c=3.329, \quad \alpha_D +0.67°)$.

Action of Ferric Chloride on Methyl d-Phenylsuccinate.

It has been shown by Meyer (*Ber.*, 1911, **44**, 2725) in the case of ethyl acetoacetate that ferric chloride exerts a direct enolising action. The behaviour of an ethyl-alcoholic solution of methyl d-phenylsuccinate towards anhydrous ferric chloride has therefore been polarimetrically investigated in the expectation that enolisation, if induced at the asymmetric carbon atom, would betray itself by racemisation. The solutions, however, were found to be optically stable under these conditions.

Methyl d-phenylsuccinate (0.4869 gram) was dissolved in ethyl alcohol and the solution made up to 20 c.c.; a portion of this solution had $\alpha_D +6.73°$ when examined in a 2-dcm. tube, and this value had not changed at the end of forty hours after the addition of a small quantity of ferric chloride. A further portion of the latter substance was added, and the solution allowed to remain at the temperature of the laboratory during nine days, at the end of which period the ester was isolated and examined in ethyl-alcoholic solution; it had $[\alpha]_D +129.8°$, whereas the value $+138.2°$ had been determined for the original specimen.

Possible Enolisation of Methyl Phenylsuccinate in Solution.

Methyl d-phenylsuccinate (0.5369 gram) and methyl r-phenylsuccinate (0.4496 gram) were separately dissolved in methyl alcohol

(20 c.c.) and titrated with an $N/10$-solution of bromine in the same solvent until a faint, permanent, yellow coloration was produced; 0·55 c.c. of bromine was required in each case, whilst in a blank experiment 0·60 c.c. was necessary.

Methyl d-phenylsuccinate (0·3292 gram) was dissolved in a well-cooled methyl-alcoholic solution of sodium methoxide, and the product poured into an excess of a solution of bromine in methyl alcohol containing hydrogen chloride. Excess of bromine was removed by the addition of β-naphthol dissolved in methyl alcohol, and the resulting solution warmed after addition of aqueous potassium iodide (10 per cent.). The liberated iodine required 0·3 c.c. of $N/10$-sodium thiosulphate solution, this quantity being the same as that required in a blank experiment.

XXV.—*Synthesis of 3:4-Dihydroxyphenanthrene (Morphol) and of 3:4-Phenanthraquinone.*

By GEORGE BARGER.

Two years ago a note was published (T., 1916, **109**, 568) describing the preparation of 3-phenanthrol-4-aldehyde, first carried out at my suggestion by a former pupil, the late J. W. Smith. As there indicated, I was able to deduce the constitution of the aldehyde from its conversion into 3:4-dihydroxyphenanthrene (morphol). From this, 3:4-phenanthraquinone was subsequently obtained, and since there has been no opportunity of further experiment in this direction, the preparation of these two compounds is described below. Morphol had not yet been synthesised, and was only known as a degradation product of morphine, for although Pschorr and Simuleanu (*Ber.*, 1900, **33**, 1810) prepared its dimethyl ether by Pschorr's well-known general method, they were unable to demethylate this compound without reduction; on boiling with hydriodic acid they only obtained 3-phenanthrol.

3 : 4-*Dihydroxyphenanthrene* (Morphol).

Ortho- and para-hydroxyaldehydes may be converted, often quantitatively, into the corresponding diphenols by a reaction due to Dakin (P., 1909, **25**, 194; *Amer. Chem. J.*, 1909, **42**, 477). In spite of its convenience and wide applicability, this reaction has, strangely enough, received very little attention. Dakin dissolves the aldehyde in one equivalent of sodium hydroxide and adds a molecular proportion of dilute hydrogen peroxide, when oxidation takes place at once with distinct evolution of heat. On applying the reaction to 3-phenanthrolaldehyde, the sparing solubility of the sodium salt made it necessary to work in very dilute solution, and only a minute quantity of the diphenanthrol was at first obtained. This difficulty was readily overcome by working in pyridine solution and limiting the amount of water as far as possible by the use of highly concentrated potassium hydroxide and hydrogen peroxide, as follows.

3-Phenanthrolaldehyde (1·11 grams) was dissolved in pyridine (10 c.c.) in a flask provided with a dropping funnel and exit tube, and after the air had been displaced by hydrogen, 0·55 c.c. of 30·8 per cent. hydrogen peroxide and then 0·45 c.c. of 12·5 *N*-potassium hydroxide were added through the tap funnel, which was washed out by a few drops of water. The addition of the potassium hydroxide caused a considerable rise in temperature (but hydrogen peroxide alone, with pyridine, does not react). After boiling for a few seconds, the solution was cooled and excess of hydrochloric acid was added through the funnel. The solution was then extracted with ether, and the ethereal extract washed free from pyridine with acid. On evaporation of the ether, the dihydroxyphenanthrene crystallised; the yield of the crude product was 1·05 grams. It was dissolved in 5 c.c. of boiling benzene, when, on cooling, 0·61 gram separated in almost colourless crystals, and a further 0·22 gram was obtained by adding light petroleum to the mother liquor, the total yield of pure substance thus amounting to 80 per cent. of the theoretical. The substance so obtained was very sensitive to oxidation; it instantly reduced silver nitrate in neutral solution at the ordinary temperature. A trace of ferric chloride gave a reddish-brown coloration, but excess caused oxidation. It was recrystallised from water and from petroleum, b. p. 80—90°, and then melted at 142—143°, so that it seemed to be identical with morphol (O. Fischer and Vongerichten, *Ber.*, 1886, **19**, 793, give 143°). By recrystallisation, it was obtained almost,

but not quite colourless. A perfectly colourless specimen resulted on sublimation in the vacuum of a Gaede pump at 130°, but the sublimate melted at 142°. On acetylation by boiling with acetic anhydride and a trace of sulphuric acid, an acetyl compound was obtained, which, after crystallisation from petroleum, b. p. 80—90°, and then from methyl alcohol, melted at 158° (O. Fischer and Vongerichten give 159° as the melting point of diacetylmorphol).

Since no morphol was available for direct comparison, the diphenol was methylated in order to provide a conclusive proof of its identity, for both the possible dimethyl ethers, 2:3- and 3:4-dimethoxyphenanthrene, have been synthesised by Pschorr and his pupils.

The crude oxidation product from 1·11 grams of the hydroxy-aldehyde was dissolved in 10 c.c. of methyl alcohol and 0·85 c.c. of methyl sulphate (2 molecular proportions), and 0·72 c.c. of 12·5N-potassium hydroxide were added alternately four times. After adding ether, washing with sodium hydroxide, drying, and evaporating the ether, the residue was distilled twice under 12 mm. pressure. At first, crystallisation could not be induced, but a trace crystallised from methyl alcohol on spontaneous evaporation of the solvent, and on adding this to the main bulk, the whole solidified almost completely. The crystals were drained on a tile, the yield was 0·3 gram. When recrystallised from methyl alcohol by evaporation at the ordinary temperature, narrow, rectangular plates were obtained melting at 45°. The picrate formed ruby-red crystals melting at 105—106°, and the dibromo-derivative colourless needles melting at 124—125°. The melting points of 3:4-dimethoxyphenanthrene, its picrate, and its dibromo-derivative are given by Pschorr and Simuleanu (*Ber.*, 1900, **33**, 1810) as 44°, 105—106°, and 124—125° respectively, and those of the corresponding 2:3-derivatives by Pschorr and Buckow (*Ber.*, 1900, **33**, 1829) as 131°, 127—128°, and 160° respectively, so that the diphenol is identified with certainty as 3:4-dihydroxyphenanthrene and the aldehyde, from which it is derived, as 3-phenanthrol-4-aldehyde.

3:4-*Phenanthraquinone*, $C_{14}H_8O_2$

Having found a comparatively ready method of preparing morphol, I was able to oxidise it to the corresponding quinone by Willstätter and Pfannenstiehl's method (*Ber.*, 1904, **37**, 4744). Five grams of silver nitrate were decomposed in a stoppered cylinder with the calculated quantity of sodium hydroxide, and the silver oxide was washed by decantation twelve times with water, six

times with acetone, and six times with dry ether. Then an ethereal solution of 0·8 gram of morphol was added, together with 2 grams of anhydrous sodium sulphate, and the mixture was shaken for fifteen seconds. A blood-red solution was formed at once, and, after settling, was decanted; the silver oxide was extracted repeatedly with ether until the solvent was no longer coloured red. On evaporation, the quinone crystallised. It was dissolved in 25 c.c. of boiling benzene, when, on cooling, 0·52 gram separated, or 65 per cent. of the theoretical. A little more was obtained by concentrating the mother liquor and adding light petroleum. 3 : 4-*Phenanthraquinone* was thus obtained in brilliant red, short, pointed prisms. The melting point is not sharp; at 125—130° the substance blackens, and on rapid heating melts in the neighbourhood of 132—133°:

0·1412 (dried at 100°) gave 0·4167 CO_2 and 0·0501 H_2O. $C = 80·5$; $H = 3·9$.

$C_{14}H_8O_2$ requires $C = 80·8$; $H = 3·9$ per cent.

The substance is a true derivative of *o*-benzoquinone, resembling 1 : 2-naphthaquinone rather than 9 : 10-phenanthraquinone in colour and instability. It further differs from 9 : 10-phenanthraquinone in not yielding Laubenheimer's reaction.

It is at once reduced by sulphurous acid to morphol. In the oxidation of the latter with silver oxide, no isomeric colourless form of the quinone could be observed, as in the case of *o*-benzoquinone (Willstätter and Müller, *Ber.*, 1908, **41**, 2580). It was easy to repeat their experiments with catechol, but not with morphol.

LISTER INSTITUTE OF PREVENTIVE MEDICINE,
    CHELSEA GARDENS, LONDON, S.W.   [*Received, March 19th*, 1918.]

XXVI.—*The Alkaloids of Ipecacuanha.   Part III.*

By Frank Lee Pyman.

In the previous paper of this series (T., 1917, **111**, 424), it was shown that O-methylpsychotrine gave a mixture containing emetine and *iso*emetine* on reduction. The formation of *iso*emetine was demonstrated by the isolation of its benzoyl derivative, for neither *iso*emetine nor any of its salts had at that time been obtained in a crystalline form. Later, however, the *hydrobromide* became crystalline, and was readily purified by crystallisation from water, and, from the pure salt, the *base, hydrochloride,* and *hydrogen oxalate* were prepared in the usual manner, and also obtained in crystalline form. On benzoylation, the base gave the benzoyl*iso*emetine previously described. Since emetine and *iso*emetine are produced by the reduction of methylpsychotrine, it was to be expected that *iso*emetine, like emetine, could be oxidised to methylpsychotrine and rubremetine, and this proved to be the case. The view that emetine and *iso*emetine are stereoisomerides was thus confirmed, and it appeared to be of interest to determine whether an equilibrium between the two bases could be established by boiling with amyl alcohol and sodium amyloxide. Experiments to this end were unsuccessful, for, after fourteen hours' boiling, no evidence of partial racemisation was obtained, each base being recovered unchanged except in so far as it had been hydrolysed to phenolic bases.

The fact that psychotrine gives cephaeline and *iso*cephaeline on reduction, whilst the methyl ether of psychotrine gives emetine and *iso*emetine, indicated the probability that *iso*emetine was the methyl ether of *iso*cephaeline, and this has now been proved by preparing *iso*emetine by the methylation of *iso*cephaeline.

When methylated under suitable conditions, *iso*emetine gives a well-crystallised *N*-methyl derivative, N-*methyl*iso*emetine,* which proves to be the O-methyl ether of the isomeride of *N*-methylcephaeline previously described (T., 1914, **105**, 1624); this substance is therefore N-*methyl*iso*cephaeline.*

* The term *iso*emetine is clearly appropriate to this compound, which is the methyl ether of the *iso*cephaeline described in 1914 (Carr and Pyman, T., 1914, **105**, 1591), and the parent of the substance already named benzoyl-*iso*emetine (Pyman, T., 1917, **111**, 424). It has since been employed by Karrer (*Ber.*, 1917, **50**, 582) for a reduction product of rubremetine. Whilst the coincidence is unfortunate, it does not appear to be important, for Karrer's '*iso*emetine '—an amorphous base from which no crystalline derivatives were prepared—is probably a mixture of stereoisomerides.

Complete methylation of *iso*emetine yields a well-crystallised N-*methyl*isoemetine *methiodide*, which is accompanied by an amorphous salt. This is probably a mixture of the two stereoisomeric methiodides of *N*-methyl*iso*emetine, the isomerism of which depends on the presence of an asymmetric nitrogen atom, for it is shown later that the complete methylation of emetine leads to a similar result. This view is borne out by the fact that the crystalline and amorphous salts give N-*methyl*isoemetine*methine* in equally good yield when converted into the corresponding methohydroxides and evaporated in a vacuum. This methine, like that of emetine, crystallises well as the neutral *oxalate*, and also forms a well-crystallised *methiodide*. So far, attempts to effect its further degradation have not led to crystalline products.

The connexion between the compounds described above and their relation to the compounds described in the previous papers is shown in the diagram on p. 225.

Reference has been made above to the formation of two stereoisomeric methiodides by the complete methylation of emetine. This operation, which consists in heating emetine with methyl iodide and aqueous sodium carbonate, has been carried out previously by several authors, but hitherto only one methiodide has been isolated, although the formation of "by-products" has been observed. In view of the fact that emetine contains a tertiary nitrogen atom common to two ring complexes, the formation of two stereoisomeric *N*-methylemetine methiodides owing their separate existence to the asymmetry of this nitrogen atom appeared to be possible. On experiment, it was found that the product of the reaction gave, besides the previously known methiodide, which melts at 225—226° (corr.) and has $[a]_D -10°$, a stereoisomeride, which melts at 262° (corr.) and has $[a]_D +68°$. Proof that this is, in fact, a stereoisomeric *N*-methylemetine methiodide, and not a derivative of some impurity in the emetine employed, is afforded by the fact that it yields the same methine as does the previously known methiodide. In accordance with the usual practice (compare Scholtz, *Ber.*, 1905, **38**, 595; Voss and Gadamer, *Arch. Pharm.*, 1910, **248**, 43; Jowett and Pyman, T., 1913, **103**, 290), the salt of lower melting point is termed the α-salt, that of higher melting point the β-salt. In previous cases, it has been possible to convert the α-salt into the β-salt by heating it above its melting point. α-*N*-Methylemetine methiodide, however, effervesces at its melting point and probably undergoes decomposition, for none of the β-salt could be isolated from the reaction product.

The remarkable influence of stereochemical structure on physiological action, which has been observed in many other cases, is

apparent in the case of emetine and *iso*emetine, which differ only in the sign of one asymmetric carbon atom.

Dr. H. H. Dale, F.R.S., of the staff of the Medical Research Committee, has kindly determined the relative toxicity of these compounds, and finds that *iso*emetine is rather less than half as toxic as emetine. The results of intravenous administration of different doses of their hydrochlorides to rabbits were as follows:

Emetine hydrochloride.			isoEmetine hydrochloride.		
4·25 mgm.* per kilo.—All died.			9·0 mgm.* per kilo.—All died.		
4·0	,,	,, —4 died out of 5.	8·5	,,	,, —4 died out of 6.
3·75	,,	,, —1 died out of 4.	8·25	,,	,, —3 died out of 6.
3·5 or less	,,	—All lived.	8·0	,,	,, —1 died out of 4.
			7·5 or less	,,	—All lived.

* Of the anhydrous salt.

With both compounds, death resulted from acute heart failure. It was also found that *iso*emetine was practically non-emetic for cats.

A clinical trial of *iso*emetine has been carried out by Dr. G. C. Low; to whom the author's thanks are due. Whilst emetine given in amœbic dysentery nauseates the patient, but brings about the elimination of the amœbæ, Dr. Low finds that *iso*emetine is well tolerated in comparatively large doses, but does not appear to have any effect on the amœbæ.

Experimental.

Isolation of isoEmetine.

*iso*Emetine occurs together with emetine and base "C" amongst the reduction products of methylpsychotrine. In order to isolate it, the syrupy base recovered from the mother liquors of emetine hydrobromide (T., 1917, **111**, 439, line 10) is dissolved in alcohol (2 parts) and mixed with a solution of hydrated oxalic acid (0·5 part) in alcohol (5 parts), and kept for several days, when a spongy, crystalline mass slowly separates. This is collected and washed with alcohol, when crude *iso*emetine hydrogen oxalate remains. Further quantities remain in the mother liquors from the crystallisation of the hydrogen oxalate of base "C" (*ibid.*, p. 438). The crude hydrogen oxalate is dissolved in water, and the base regenerated into ether by sodium hydroxide; after removing the solvent, the residue is dissolved in a slight excess of dilute hydrobromic acid, digested with animal charcoal, and filtered, when *iso*emetine hydrobromide separates on inoculating and cooling, and is purified readily by recrystallisation from water.

N-Methyl*iso*cephaeline,
$C_{29}H_{40}O_4N_2$

*iso*Cephaeline,
$C_{28}H_{38}O_4N_2$

N-Methyl*iso*emetine,
$C_{30}H_{42}O_4N_2$

N-Methyl*iso*emetine methiodide,
$C_{32}H_{48}O_4N_2I_2$

N-Methyl*iso*emetinemethine,
$C_{32}H_{46}O_4N_2$

*iso*Emetine,
$C_{29}H_{40}O_4N_2$

Psychotrine,*
$C_{28}H_{36}O_4N_2$

O-Methylpsychotrine,*
$C_{29}H_{38}O_4N_2$

Rubremetine hydrochloride,
$C_{29}H_{38}O_4N_2Cl$

Cephaeline,*
$C_{28}H_{38}O_4N_2$

Emetine,*
$C_{29}H_{40}O_4N_2$

N-Methylcephaeline,
$C_{29}H_{40}O_4N_2$

N-Methylemetine,
$C_{30}H_{42}O_4N_2$

N-Methylemetine methiodide,
$C_{32}H_{48}O_4N_2I_2$

N-Methylemetinemethine,
$C_{32}H_{46}O_4N_2$

* Occurs naturally.

isoEmetine, $C_{29}H_{40}O_4N_2$.

The base crystallises from ether in characteristic disks (circular plates) formed of radiating needles, containing $1H_2O$, which is not completely lost in a vacuum. The air-dried base softens at 92° and melts at 97—98° (corr.); the same form and melting point were observed after recrystallisation of the base from ethyl acetate.

Found, in air-dried base (from ether): $C = 69·7$; $H = 8·5$; loss in a vacuum $= 2·5$.

$C_{29}H_{40}O_4N_2,H_2O$ (498·5) requires $C = 69·9$; $H = 8·5$; loss of $1H_2O = 3·6$ per cent.

The base is insoluble in water, but easily soluble in the usual organic solvents with the exception of light petroleum. Its colour-reactions with Fröhde's reagent (green) and sodium diazobenzene-p-sulphonate (red in the presence of sodium carbonate, little changed on the addition of dilute hydrochloric acid) are identical with those given by emetine.

The specific rotatory power of the base, dried in a vacuum, was determined in chloroform solution:

$$a_D - 3·33°; \quad c = 3·514; \quad l - 2\text{-dcm.}; \quad [a]_D - 47·4°.$$

The *hydrochloride* was obtained as a mass of small needles by neutralising the base with aqueous hydrochloric acid, evaporating the solution to dryness, and boiling the residue with absolute alcohol. It melts and decomposes at 310° (corr.), and is easily soluble in water, but almost insoluble in absolute alcohol.

This salt is almost anhydrous, losing only 0·5 per cent. at 100°.

Found in dried salt: $C = 62·6$; $H = 7·7$; $Cl = 12·8$.

$C_{29}H_{40}O_4N_2,2HCl$ (553·4) requires $C = 62·9$; $H = 7·7$; $Cl = 12·8$ per cent.

The specific rotatory power of this salt was determined in aqueous solution, and found to be negative at high, but positive at low concentrations:

$$a_D - 4·70°; \quad c = 15·07; \quad l = 2\text{-dcm.}; \quad [a]_D - 15·6°.$$
$$a_D - 0·87°; \quad c = 8·134; \quad l = 2\text{-dcm.}; \quad [a]_D - 5·3°.$$
$$a_D + 0·38°; \quad c = 4·092; \quad l = 2\text{-dcm.}; \quad [a]_D + 4·6°.$$
$$a_D + 0·35°; \quad c = 2·259; \quad l = 2\text{-dcm.}; \quad [a]_D + 7·7°.$$
$$a_D + 0·23°; \quad c = 0·909; \quad l = 2\text{-dcm.}; \quad [a]_D + 12·7°.$$

The *hydrobromide* crystallises from water in well-formed prisms, which contain $4H_2O$. It is easily soluble in hot, but sparingly so (1—2 per cent.) in cold water. After drying in a vacuum, it softens from 215° and gradually becomes transparent without flowing, up to 220° (corr.).

Found, in air-dried salt: $C = 48.8$; $H - 7.2$; loss in a vacuum, 10·1, 10·0, 10·0.

$C_{29}H_{40}O_4N_2,2HBr,4H_2O$ (714·4) requires $C = 48.7$; $H = 7.1$; $H_2O = 10.1$ per cent.

Found, in dried salt: $C = 54.0$, 54·4; $H = 6.7$, 6·8; $Br = 24.7$.

$C_{29}H_{40}O_4N_2,2HBr$ (642·3) requires $C = 54.2$; $H = 6.6$; $Br = 24.9$ per cent.

The specific rotatory power of the hydrated salt was determined in aqueous solution:

$$\alpha_D + 0.54°; \ c = 4.153; \ l = 2\text{-dcm.}; \ [\alpha]_D + 6.5°.$$
$$\alpha_D + 0.42°; \ c = 1.989; \ l = 2\text{-dcm.}; \ [\alpha]_D + 10.5°.$$

The *hydrogen oxalate* crystallises from water in colourless prisms, which contain $5H_2O$, and melt at 92—95° (corr.). After drying at 100°, it has no definite melting point, but softens from about 150° and effervesces at about 165° (corr.). It is easily soluble in water or alcohol, but its solution in the latter deposits a colourless, spongy mass on keeping.

Found, in air-dried salt: loss in a vacuum = 11·8.

$C_{29}H_{40}O_4N_2,2C_2H_2O_4,5H_2O$ (750·6) requires $H_2O = 12.0$ per cent.

Found, air dried in a vacuum: $C = 59.8$, 60·1; $H = 7.0$, 6·8.

$C_{29}H_{40}O_4N_2,2C_2H_2O_4$ (660·5) requires $C = 60.0$; $H = 6.7$ per cent.

The specific rotatory power was determined in aqueous solution:

$$\alpha_D + 0.25°; \ c = 8.019; \ l = 2\text{-dcm.}; \ [\alpha]_D + 1.6°.$$
$$\alpha_D + 0.50°; \ c = 3.856; \ l = 2\text{-dcm.}; \ [\alpha]_D + 6.5°.$$
$$\alpha_D + 0.50°; \ c = 2.958; \ l = 2\text{-dcm.}; \ [\alpha]_D + 8.5°.$$
$$\alpha_D + 0.33°; \ c = 1.454; \ l = 2\text{-dcm.}; \ [\alpha]_D + 11.3°.$$

Methylation of iso*Cephaeline. Formation of* iso*Emetine.*

0·4 Gram of *iso*cephaeline (T., 1914, **105**, 1626) was dissolved in a solution of 0·05 gram of sodium in 35 c.c. of fusel oil boiling at 130—133°; 0·2 gram of anhydrous sodium methyl sulphate was added, and the mixture boiled for one and a-half hours under a reflux condenser. After acidifying with hydrochloric acid, the liquor was distilled with steam to remove the fusel oil, and the alkaloids were then regenerated to ether by means of sodium carbonate. The ethereal solution was extracted with dilute aqueous sodium hydroxide, which removed 0·15 gram of unchanged *iso*-cephaeline, evaporated to dryness, and converted into the hydro-bromide, when 0·17 gram of crude *iso*emetine hydrobromide was obtained. After recrystallisation from water, this salt formed prismatic needles, having the melting point previously recorded, either alone or mixed with *iso*emetine hydrobromide resulting from

the reduction of methylpsychotrine. For further identification, the base was regenerated from the hydrobromide, when it crystallised from ether in the characteristic disks, melting at 97—98° (corr.), both alone and when mixed with a specimen of the base resulting from the reduction of methylpsychotrine.

Methylation of isoEmetine. Formation of N-Methylisoemetine and Isolation of Benzoylisoemetine.

isoEmetine was methylated by methyl sulphate and sodium methoxide, the resulting mixture of N-methylisoemetine and unchanged isoemetine being separated by removing the latter as the benzoyl derivative, the hydrochloride of which can be extracted from aqueous solution by chloroform. The method is precisely similar to that employed for the methylation of emetine (T., 1914, 105, 1617), to which reference may be made for further details.

isoEmetine, regenerated from 7·2 grams of the hydrated hydrobromide, was dissolved in a solution of 0·5 gram of sodium in 25 c.c. of methyl alcohol and treated with 2·5 grams of methyl sulphate, when 1·3 grams of N-methylisoemetine and 2·1 grams of benzoylisoemetine were obtained.

N-Methylisoemetine crystallises from ether in clear, colourless, square tablets with bevelled edges. It melts at 152—153° (corr.), and crystallises again on cooling. It suffers no loss in a vacuum.

Found : C = 72·8 ; H = 8·5.

$C_{30}H_{42}O_4N_2$ (494·5) requires C = 72·9 ; H = 8·6 per cent.

The specific rotatory power was determined in chloroform solution :

$\alpha_D - 2·55°$; $c = 2·550$; $l = 2$-dcm. ; $[\alpha]_D - 50·0°$.

Benzoylisoemetine proved to be identical with the substance previously described under this name (T., 1917, 111, 439). It formed colourless prismatic needles from acetone, which melted at 207—208° (corr.) alone or when mixed with the preparation to which reference has been made. The specific rotatory power in chloroform solution was found to be $[\alpha]_D + 47·3°$ ($c = 2·833$).

Methylation of N-Methylisocephaeline. Formation of N-Methylisoemetine.

The isomeride (T., 1914, 107, 1624) of N-methylcephaeline yields N-methylisoemetine on methylation, and is therefore N-methylisocephaeline.

Two grams of the pure isomeride, melting at 196—197° (corr.), were dissolved in a solution of 0·5 gram of sodium in 50 c.c. of

fusel oil, boiling at 130—133°, and boiled for two hours under
a reflux condenser with 1·25 grams of anhydrous sodium methyl
sulphate. On working up the product in the usual way (compare,
for instance, T., 1914, **107**, 1623); 1·4 grams of the phenolic base
were recovered, and 0·23 gram of *N*-methyl*iso*emetine was obtained.
This base melted at 152—153° (corr.) alone or when mixed, with
the methylation product of *iso*emetine; the specific rotatory power
in chloroform solution was found to be $[\alpha]_D -47\cdot6°$ ($c=1\cdot125$).

N-*Methyl*isoemetine *Methiodide*.

Twenty-five grams of *iso*emetine hydrobromide were dissolved in
625 c.c. of hot water, cooled, mixed with 50 c.c. of methyl iodide
and 25 grams of anhydrous sodium carbonate, and heated on the
water-bath. After one and three-quarter hours, the insoluble
matter, which was viscous and amorphous at first, had become
crystalline, and was collected. It amounted to 21·3 grams, and
formed colourless, well-defined, oblong prisms which melted at
290—292° (corr.) after drying at 100°. This salt is very sparingly
soluble in cold water.

Found, in air-dried salt, loss in a vacuum $=2\cdot4$; in dried salt,
$I=32\cdot4$.

$\quad$ $C_{32}H_{46}O_4N_2I_2,H_2O$ (796·4) requires $H_2O=2\cdot3$ per cent.
$\quad\quad$ $C_{32}O_{48}O_4N_2I_2$ (778·4) requires $I=32\cdot6$ per cent.

The specific rotatory power of the hydrated salt was determined
in aqueous solution :

$\quad\quad$ $\alpha_D + 0\cdot6°$; $c=0\cdot324$; $l=2$-dcm. ; $[\alpha]_D + 92\cdot6°$.

The mother liquors from the crystalline methiodide were con-
centrated, and deposited 6·5 grams of pale orange-brown resin,
which became quite hard, but was not obtained in a crystalline
form. The crystalline and amorphous salts were found to give
the methine in approximately equal yield.

N-*Methyl*isoemetinemethine, $C_{32}H_{46}O_4N_2$.

29·2 Grams of *iso*emetine hydrobromide were converted into
methyl*iso*emetine methiodide by the method described above, and
the combined crystalline and amorphous methiodides were con-
verted into the anhydro-base by the method employed for methyl-
emetinemethine (T., 1917, **111**, 445). The crude methine was
neutralised with 20 per cent. aqueous oxalic acid, and gave 21·1
grams of neutral oxalate in several crops, that is, 75·4 per cent.
of the theoretical yield.

*Methyl*isoemetinemethine *oxalate* crystallises from water in

colourless prisms of an elongated diamond shape which are very easily soluble in water. The air-dried salt contains $4H_2O$ and melts at 122—127° (corr.); after drying at 100°, the salt melts at 133—134° (corr.).

Found, in air-dried salt: $H_2O = 10·8$, 10·7.

$C_{32}H_{46}O_4N_2,C_2H_2O_4,4H_2O$ (684·6) requires $H_2O = 10·5$ per cent.

Found, in air-dried salt: $C = 66·4$, 66·4, 66·5, 66·5; $H = 7·9$, 7·9, 7·9, 7·9.

$C_{32}H_{46}O_4N_2,C_2H_2O_4$ (612·6) requires $C = 66·6$; $H = 7·9$ per cent.

The specific rotatory power of this salt was determined in aqueous solution:

$$a_D + 0·35°; \quad c = 4·153; \quad l = 2\text{-dcm.}; \quad [a]_D + 4·2°.$$

Methylisoemetinemethine methiodide separates as a crystalline powder when a concentrated ethereal solution of the methine, prepared by regeneration from the pure oxalate, is warmed with methyl iodide. The salt, so prepared, began to sinter at 155° and effervesced at 163° (corr.); when moistened with cold water, it first became gummy and then crystallised; it appeared to contain methyl iodide of crystallisation, for when it was added to boiling water effervescence took place, and an odour of methyl iodide was observed. The hot aqueous solution deposited the salt on cooling in silky needles, which melt at 178° (corr.) after drying at 100°, and effervesce at about 180°.

Found, in air-dried salt: loss at 110° = 4·0.

$C_{34}H_{52}O_4N_2I_2,2H_2O$ (842·4) requires $H_2O = 4·3$ per cent.

Found, in dried salt: $I = 31·6$.

$C_{34}H_{52}O_4N_2I_2$ (806·4) requires $I = 31·5$ per cent.

Oxidation of isoEmetine. Formation of Methylpsychotrine and Rubremetine.

(1) *With One Molecular Proportion of Iodine.*—This oxidation was carried out essentially in the same way as that of emetine (T., 1917, **111**, 434). but the isolation of methylpsychotrine as hydrogen oxalate was complicated by the fact that *iso*emetine hydrogen oxalate also crystallises from moist alcohol, whereas emetine hydrogen oxalate does not.

Twenty grams of *iso*emetine hydrobromide were recrystallised from 50 c.c. of water, when 19 grams separated. After removing this, the mother liquor gave further small crops of the same salt on concentration, and eventually a liquor which no longer deposited crystals. This was shaken with aqueous sodium hydroxide and ether, and the regenerated base, amounting to 0·04 gram, was con-

verted into the hydrogen oxalate in alcoholic solution, when 0·02 gram of colourless, somewhat spongy crystals was obtained, which, after drying at 100°, sintered at 145°, and gradually melted up to about 200°. The melting point indicates that this hydrogen oxalate did not consist wholly of methylpsychotrine hydrogen oxalate, whence the original hydrobromide contained less than 1 per cent. of methylpsychotrine.

Nine grams (part of the 19 grams) of purified *iso*emetine hydrobromide were then converted into the base and oxidised with 3·2 grams of iodine in 80 c.c. of absolute alcohol by heating for three and a-half hours at 100°.

The product was mixed with dilute sulphurous acid, evaporated to about half its volume, mixed with aqueous sodium hydroxide, and extracted with chloroform. The chloroform extract was completely extracted with dilute hydrochloric acid, dried, and distilled, when it left 2·3 grams of dark brown resin. This was extracted with small quantities of boiling water, and the filtered extracts were mixed with a small quantity of aqueous potassium iodide, when 0·9 gram of rubremetine hydriodide separated in minute red needles, which, after drying at 100°, began to melt at 177° (corr.) either alone or when mixed with rubremetine hydriodide prepared by the oxidation of emetine. The identification of the salt with rubremetine hydriodide was further confirmed by analysis. (Found, in air-dried salt, $H_2O = 13·5$; in dried salt, $I = 21·3$. Calc.: $H_2O = 13·0$; $I = 21·2$ per cent.)

The hydrochloric acid extract of the chloroform extract was mixed with aqueous sodium hydroxide and extracted with chloroform. The chloroform residue was converted into the hydrobromide, when 5·0 grams of *iso*emetine hydrobromide were recovered. The mother liquors, shaken with aqueous sodium hydroxide and ether, gave 0·7 gram of base, which was dissolved in alcohol containing 0·4 gram of hydrated oxalic acid. On inoculating with methylpsychotrine hydrogen oxalate, 0·13 gram of nearly colourless crystals, melting at 140—145° (corr.), separated. For purification, the base was regenerated from this material and again converted into hydrogen oxalate, when 0·08 gram was obtained, which melted at 145—150° (corr.), methylpsychotrine hydrogen oxalate melting at 150—155° (corr.) in the same bath, and a mixture of the two substances intermediately. The aqueous solution of the salt showed the blue fluorescence characteristic of methylpsychotrine salts. A determination of the specific rotatory power gave a low value, $[\alpha]_D + 33°$ ($c = 1$), and consequently further evidence of the identity of the substance was required. Accordingly, the base was regenerated, neutralised with dilute sulphuric

acid, and the solution evaporated to dryness, then moistened with absolute alcohol and evaporated to dryness several times. Finally, it was dissolved in a few drops of absolute alcohol and inoculated with methylpsychotrine sulphate monohydrate, when a colourless, crystalline powder separated, which melted at 245° (corr.), methyl-psychotrine sulphate melting at 248° (corr.), and a mixture of the two substances at 246° in the same bath.

(2) *With Ferric Chloride.*—Two grams of *iso*emetine hydro-chloride were oxidised with an aqueous solution of 40 grams of commercial hydrated ferric chloride, the details of manipulation being the same as previously described for the oxidation of emetine with ferric chloride (T., 1914, **105**, 1627). After crystallisation from water, 0·45 gram of crude rubremetine hydrochloride was obtained. This was purified in the manner previously described, and identified by comparison with a specimen prepared from emetine.

Action of Sodium Amyloxide on isoEmetine.

The base liberated from 3 grams of *iso*emetine hydrobromide was dissolved in a solution of 1·0 gram of sodium in 50 c.c. of fusel oil (b. p. 130—133°), and boiled for fourteen hours under a reflux condenser. After the addition of 6 c.c. of hydrochloric acid and 20 c.c. of water, the fusel oil was removed by steam distillation, and the non-phenolic and phenolic bases were recovered and separated in the usual way. The latter—amounting to 0·3 gram of yellow resin—were neglected, whilst the non-phenolic bases were found to consist almost entirely of *iso*emetine, for when treated with hydrobromic acid they gave 2·3 grams of pure *iso*emetine hydrobromide, the mother liquors containing only a trace of material.

Emetine, when treated in a similar manner, was also mainly recovered unchanged, except in so far as it had become hydrolysed, and no evidence of the formation of *iso*emetine could be obtained.

Preparation and Separation of α- and β-N-Methylemetine Methiodides.

Ten grams of emetine hydrobromide were dissolved in 250 c.c. of hot water, and the solution, after cooling to some extent, was mixed with 20 c.c. of methyl iodide and 10 grams of anhydrous sodium carbonate. It was then heated on the water-bath under a reflux condenser so that the methyl iodide boiled. After three hours crystals began to form, and gradually increased in quantity; after boiling for a fourth hour, the excess of methyl iodide was

removed by distillation and the liquor filtered from the first crop
of crystals—8·0 grams; m. p. 210—220°; $[a]_D$ − 6°. On cooling,
the mother liquor deposited a second crop of crystals—2·6 grams;
m. p. 220—260°; $[a]_D$ + 32·4°—whilst a third fraction was obtained
by extraction with chloroform as a nearly colourless resin (0·7
gram) which deposited crystals after solution in water. After
recrystallising the first crop from water twice, the previously known
a-methiodide was obtained in a pure state; it had the melting point
previously recorded, namely, 225—226° (corr.), and formed prisms
containing between 3 and $4H_2O$. (Found: $H_2O = 7·9$. Calc.
for $3H_2O$, 6·3; for $4H_2O$, 8·5 per cent.) The specific rotatory
power was determined in aqueous solution:

$$a_D - 0·23°; \quad c = 1·145; \quad l = 2\text{-dcm.}; \quad [a]_D - 10·0°.$$

After prolonged fractional crystallisation, there were obtained
5·35 grams of this salt in a pure state, 2·6 grams less pure, melting
at 210—220°, various small crops melting between 220° and 260°,
and 0·45 gram of the pure β-methiodide.

a-N-Methylemetine methochloride was prepared from the
a-methiodide by double decomposition with silver chloride, con-
centration of the filtered solution to a syrup, and precipitation with
acetone, when it formed small, colourless needles which melted at
133° (corr.) after drying at 100°, and at 200° (corr.) after drying
at 110°.

Found, in air-dried salt: loss at 100—110° = 15·2.

$C_{32}H_{48}O_4N_2Cl_2,6H_2O$ (703·6) requires $H_2O = 15·3$ per cent.

Found, in salt dried at 100—110°: C = 64·2, 64·2; H = 8·1, 8·0.

$C_{32}H_{48}O_4N_2Cl_2$ (595·5) requires C = 64·5; H = 8·1 per cent.

The specific rotatory power of this salt was determined in aqueous
solution:

$$a_D - 0·18; \quad c = 3·986; \quad l = 2\text{-dcm.}; \quad [a]_D - 2·3°.$$
$$a_D - 0·18; \quad c = 1·993; \quad l = 2\text{-dcm.}; \quad [a]_D - 4·5°.$$

β-N-Methylemetine methiodide forms long, flat plates from water,
which melt at 262° (corr.) after drying at 100°. Like the a-salt, it
is easily soluble in hot, but very sparingly so in cold water.

Found, in air-dried salt: $H_2O = 5·2$.

$C_{32}H_{48}O_4N_2I_2,2\frac{1}{2}H_2O$ (823·4) requires $H_2O = 5·5$ per cent.

Found, in salt dried in a vacuum: C = 49·6; H = 6·3.

$C_{32}H_{48}O_4N_2I_2$ (778·4) requires C = 49·3; H = 6·2 per cent.

The specific rotatory power was determined in aqueous solution:

$$a_D + 1·15°; \quad c = 0·844; \quad l = 2\text{-dcm.}; \quad [a]_D + 68·1°.$$

Formation of N-*Methylemetinemethine from the β-Methiodide.*

0·5 Gram of the β-methiodide was converted into the methine by the method used for the α-methiodide (T., 1917, **111**, 445). The crude tertiary base, extracted by ether (0·27 gram), was dissolved in alcohol and neutralised with oxalic acid, when 0·12 gram of methylemetinemethine oxalate crystallised in prisms. It melted at 82—83° (corr.), a mixture with the salt prepared from the α-methiodide melting at the same temperature.

For further identification, the water of crystallisation was estimated (Found: $H_2O = 18·9$. Calc.: $H_2O = 18·1$ per cent.), and an approximate determination of the specific rotatory power was made [Found: $[α]_D - 19·5°$ ($c = 1·2$ in water); previously found for salt from α-methiodide, $[α]_D - 24·6$]. It was also observed that the methine from the β-methiodide gave a hydrochloride, which crystallised from absolute alcohol in plates. A similar salt had previously been obtained from the methine prepared from the α-methiodide, by the following method.

N-*Methylemetinemethine Hydrochloride.*

A quantity of the base, regenerated from the pure oxalate to ether, was dissolved in dilute hydrochloric acid and evaporated to dryness. It was next dissolved in absolute alcohol and evaporated to dryness, this operation being repeated several times. It was then dissolved in a small volume of absolute alcohol, when it separated in colourless, quadrilateral plates, which melted at 236° (corr.) after drying at 100°. This salt is very easily soluble in water.

Found, in air-dried salt: loss at 105° = 2·4, 3·7.

$C_{33}H_{46}O_4N_2,2HCl,H_2O$ (613·4) requires $H_2O = 2·9$ per cent.

Found, in salt dried at 105°: Cl = 11·5, 11·5.

$C_{32}H_{46}O_4N_2,2HCl$ (595·5) requires Cl = 11·9 per cent.

XXVII.—*The Supposed Formation of Ergotoxine Ethyl Ester from Ergotinine. A Correction.*

By GEORGE BARGER and ARTHUR JAMES EWINS.

SOME years ago (T., 1910, **97**, 284) we obtained a crystalli·ie phosphate by boiling ergotinine in alcoholic solution with phosphoric acid, and we concluded that the salt was the phosphate of ergotoxine ethyl ester. This is not so; it is the phosphate of ergotoxine itself. Ergotoxine, $C_{35}H_{41}O_6N_5$, is the hydrate of ergotoxine, $C_{35}H_{39}O_5N_5$ (Barger and Carr, T., 1907, **91**, 337), and at the time of our previous work the phosphate of ergotoxine (the first salt to be crystallised) had been obtained exclusively in the form of fine needles (T., 1910, **97**, 286, Fig. 2), whilst our supposed ester salt crystallised in broad plates (*loc. cit.*, Fig. 1). Similar differences of crystalline form were observed in the hydrochlorides (*loc. cit.*, Figs. 3 and 4), and oxalates, prepared from the two phosphates. (On the other hand, each pair of salts had approximately the same melting point.) We chiefly relied, however, on an analysis (1 per cent. more carbon than in ergotoxine phosphate, as calculated) and a Zeisel determination of the ethoxy-group. (Found, 5·97. Calc., 5·82 per cent.)

Some years later, Mr. F. H. Carr and Dr. F. L. Pyman determined the methoxy- and methylimino-groups in ergotoxine and in ergotinine, and drew the conclusion that both alkaloids contain one *O*-methyl and one *N*-methyl group. In that case we ought to have found two alkyloxy-groups in the ester, as Messrs. Carr and Pyman pointed out to us. Their determinations were as follows:

Ergotinine.—The substance was of good colour and crystalline appearance, and melted at 231°. It suffered no appreciable loss on drying even at 130°.

1. 0·4051 gave 0·1241 AgI below 180°. OMe = 4·0.
    and 0·1004 AgI above 290°. NMe = 3·1.

2. 0·3019 gave 0·0851 AgI below 180°. OMe = 3·7.
    and 0·0942 AgI above 290°. NMe = 3·9.

3. After a blank distillation of the hydriodic acid yielding 0·0053 AgI:

0·1457 gave 0·0258 AgI below 180°. OMe = 2·3.

4. After a blank distillation of the hydriodic acid yielding 0·0123 AgI:

0·4128 gave 0·0794 AgI below 180°. OMe = 2·5.
    and 0·1139 AgI above 290°. NMe = 3·4.

5. After a blank distillation of the hydriodic acid (10 c.c.) yield-
ing 0·0098 AgI and the subsequent addition of 5 c.c. of acetic
anhydride:

0·4127 gave 0·1548 AgI below 180°. OMe = 4·9.
    and 0·0688 AgI above 290°. NMe = 2·1.

6. After a blank distillation of the hydriodic acid (10 c.c.) yield-
ing 0·0218 AgI, and the subsequent addition of 5 c.c. of acetic
anhydride:

0·4130 gave 0·1401 AgI below 180°. OMe = 4·5.
    and 0·0764 AgI above 290°· NMe = 2·3.

7. Blank distillation with 10 c.c. of hydriodic acid for one hour
gave 0·0027 AgI, after addition of 5 c.c. of acetic anhydride, and
a double distillation for two hours gave 0·0183 AgI, after a further
double distillation for two and one-third hours gave 0·0025 AgI :

0·4966 gave 0·1501 AgI below 180°. OMe = 4·0.
    and 0·0713 AgI above 290°. NMe = 1·7.
    $C_{35}H_{39}O_5N_5$ requires OMe = 5·1 ; NMe = 4·8 per cent.

Ergotoxine Phosphate.—

1. 0·3976 gave 0·1204 AgI at 140—195°. OMe = 4·0.
2. 0·3926   ,,   0·1614 AgI ,, 140 —195°. OMe = 5·4.
3. 0·2302   ,,   0·0732 AgI ,, 140—195°. OMe = 4·2.
4. 0·3954 gave 0·1055 AgI below 180°. OMe = 3·5.
    and 0·0663 AgI above 290°. NMe = 2·1.
5. 0·3914 gave 0·0982 AgI below 180°. OMe = 3·3.
    and 0·0678 AgI above 290°. NMe = 2·0.
6. 0·1420 gave 0·0494 AgI below 180°. OMe = 4·6.
    and 0·0364 AgI above 290°. NMe = 3·2.

Specimen No. 1 was prepared from ergotinine, the rest from
ergot. Nos. 4–6 were dried at 100° and analysed with the
addition of acetic anhydride. The melting point was 187—188°.

0·1482. dried at 100° (mixed with CuO), gave 0·3120 CO_2 and
    0·0900 H_2O. C = 57·4 ; H = 6·8.
    $C_{35}H_{41}O_6N_5,H_3PO_4$ requires C = 57·9 ; H = 6·1 ; OMe = 4·3 ;
                NMe = 4·0 per cent.

On receipt of the above data we re-examined the action of alco-
holic phosphoric acid on ergotinine, on a larger scale than was
originally possible. We were able to transform the salt, first
obtained as needles, into plates by recrystallisation from alcohol.

One gram of ergotinine was suspended in 15 c.c. of absolute
alcohol, and rather more than one molecular proportion of syrupy
phosphoric acid was added. On heating under reflux on the water-

bath the ergotinine dissolved, but after a total heating of thirty to forty-five minutes the solution became almost solid with a mass of prismatic needles, which were collected.

The yield was 0·95 gram, or 80 per cent. of the theoretical; the melting point, 189—190°. After drying at 100°:

0·5720 gave 0·0246 AgI (two hours at 140—150°). OMe=0·56.

On recrystallisation from alcohol, plates were formed, melting at 190°, which were analysed:

0·4216 gave 0·0412 AgI (two hours at 150°). OMe=1·3.

From these experiments we conclude that the phosphate was that of ergotoxine, and that no ethyl ester grouping was present, for it would have been readily removed under the analytical conditions employed.

We next examined the action of hydriodic acid on ergotinine, using in each case 10 c.c. of acid (D 1·7) and 5 c.c. of acetic anhydride, the bath being heated for two hours at the temperature intervals indicated.

A. Ergotinine, older (less pure) specimen:

0·4127 gave 0·1259 AgI at 150—195° and 0·0389 AgI at 340—350°. Total AgI=0·1648. OMe=5·3 or NMe=4·9.

B. Ergotinine, purer specimen:

0·4129 gave 0·0105 AgI at 140—145°, 0·1333 AgI at 180—200°, and 0·0303 AgI at 300—370°. Total AgI=0·1741. OMe=5·6 or NMe=5·2.

$C_{35}H_{39}O_5N_5$ requires OMe=5·1; NMe=4·8 per cent.

We have calculated our results from the total silver iodide formed, for we believe that only one methyl group is present, and think that this methyl group is attached to nitrogen. Messrs. Carr and Pyman's six analyses, in which heating was continued to 290°, when calculated as NMe only, give the mean 6·4 per cent., which is one-third more than the theoretical. In our opinion the amount of silver iodide is, however, insufficient to account for a methoxy-as well as a methylimino-group. There is abundant evidence that many methylimino-groups give off part of their methyl as methyl iodide on merely boiling with hydriodic acid, particularly if carbonyl groups are adjacent (Busch, *Ber.*, 1902, **35**, 1565; Goldschmiedt and Hönigschmid, *Ber.*, 1903, **36**, 1850; *Monatsh.*, 1906, 27, 849; Kirpal, *Ber.*, 1908, **41**, 819). Decker (*Ber.*, 1903, **36**, 2895) has pointed out that in this way *N*-alkyl may be mistaken for *O*-alkyl, and Herzig (*Monatsh.*, 1908, **29**, 295) states that with nitrogenous substances, unless the formation of silver iodide begins soon after the hydriodic acid boils, and proceeds rapidly to an end, it is unsafe to conclude that a methoxyl group is present. In

our own experiments the evolution of methyl iodide from the boiling acid was slow and incomplete, whence our conclusion, that ergotinine and ergotoxine contain one N-methyl group, but no methoxy-group.

We desire to thank Messrs. Carr and Pyman for having directed our attention to the error in our former paper, and for having placed their analytical results at our disposal.

LISTER INSTITUTE OF PREVENTIVE MEDICINE,
    CHELSEA GARDENS, LONDON, S.W.   [Received, March 16th, 1918.]

XXVIII.—Interaction of Formaldehyde and Carbamide.

By AUGUSTUS EDWARD DIXON.

IN a paper by Dixon and Taylor on the interaction of aldehydes and thiocarbamides (T., 1916, **109**, 1244), it is mentioned in passing that a molecular mixture of carbamide and formaldehyde, when condensed by means of hydrochloric acid, yielded a substance, apparently identical with the methylenecarbamide obtained by Hemmelmayr (*Monatsh.*, 1891, **12**, 94), from carbamide and chloromethyl alcohol. Subsequently—but not until most of the present investigation had been completed—it was learned that several chemists have already studied the interaction between carbamide and formaldehyde (see, for example, Hoelzer, *Ber.*, 1884, **17**, 659; Tollens, *ibid.*, 1896, **29**, 275; Goldschmidt, *ibid.*, 2439; *Chem. Zeit.*, 1897, **21**, 460, 586; Einhorn and Hamburger, *Ber.*, 1908, **41**, 24). In one case only is it necessary to comment on the results.

According to Goldschmidt, carbamide yields, with "excess" of formaldehyde, a compound, $C_5H_{10}O_3N_4$ (that is, $2CH_4ON_2 + 3CH_2O - 2H_2O$), which is formed alike in the presence or in the absence of acids *; and as the yield is theoretical, he concludes that carbamide may thus be determined quantitatively. With these statements, the author's experience does not quite tally; for, in an acidified mixture, the precipitate may not be formed quantitatively; it may have a different composition, or it may not be formed at all. Moreover, in a neutral mixture of the components, even after six months' keeping, no sign of condensation was observed (Expt. 1).

From a slightly acidified solution of carbamide (1 mol.), the condensate, with 0·75 mol. of formaldehyde, is methylenecarbamide;

---

* Presumably, this means in a neutral solution.

with 1 mol. of formaldehyde it is slightly contaminated with Goldschmidt's compound. With $1\frac{1}{2}$ mols. of formaldehyde, and thenceforward up to well beyond 2 mols., the latter compound is the sole product. Further increase of the formaldehyde ratio diminishes the yield, which, at 4 mols., is small, the product being a substance, $C_5H_{12}O_4N_4$; whilst, with 11 mols., condensation ceases.

The precipitates obtained by "catalysing" solutions of carbamide containing variable proportions of formaldehyde, although differing, it may be, largely in composition, exhibit a close general resemblance. They occur in minute, white granules, apparently amorphous, each of which, in plane-polarised light, usually displays a black cross, like that of certain starches. Practically insoluble in all the common solvents, and in cold, dilute mineral acids, they are resolved by heating with the latter into formaldehyde and carbamide; infusible, they decompose at a high temperature, considerably variable with the duration of the preliminary heating (somewhere in the neighbourhood of 240—250°, uncorr.).

From these facts it is concluded that the so-called methylene-carbamide cannot properly be represented by the simple formula, $CO\diagdown_{NH}^{NH}\diagup CH_2$, but is a dimeride, containing, like Goldschmidt's compound, two carbamide residues in the molecule. Its configuration may be represented as $CO\diagdown_{NH\cdot CH_2\cdot NH}^{NH\cdot CH_2\cdot NH}\diagup CO$ (I), Goldschmidt's compound being the methylol derivative,

$$CO\diagdown_{N(CH_2\cdot OH)\cdot CH_2\cdot NH}^{NH————CH_2\cdot NH}\diagup CO \text{ (II)},$$
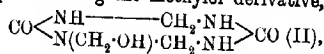
whilst the substance, $C_5H_{12}O_4N_4$, mentioned above, is probably similar, that is, $CO\diagdown_{NH\cdot CH_2\cdot OH \ \ HO\cdot CH_2\cdot NH}^{NH————CH_2————NH}\diagup CO$ (III). The formula, $CO(NMe\cdot CO\cdot NH_2)_2$, proposed by Goldschmidt (*loc. pr. cit.*) for his compound does not seem to be in harmony with its decomposition into carbamide and formaldehyde by dilute acids; it is slowly attacked, too, by hot alkalis, with the evolution of ammonia, but no methylamine was detected.

Ready-formed "methylenecarbamide," when kept in contact with formalin, did not combine with it, to yield the compound II above, nor did this, under like conditions, give the possible derivative, $CO\diagdown_{NH\cdot CH_2\cdot(CH_2\cdot OH)N}^{N(CH_2\cdot OH)\cdot CH_2\cdot NH}\diagup CO$ (IV); the last compound, in fact, has not been isolated, even in circumstances apparently favourable.

From a neutral solution of carbamide (1 mol.) in formalin (1 mol.), methylolcarbamide, together with a little dimethylolcarbamide, is deposited on concentration in a vacuum over sulphuric acid. The former compound, it would seem, is a near precursor of

L*

" methylenecarbamide "; for, such a solution, if kept for one-and-a-half hours, so as to give the components a little time to combine before treatment with acid (they do not quickly unite in quantitative amount), began to condense nearly twice as soon as a mixture, otherwise similar, but freshly prepared. Moreover, when ready-formed methylolcarbamide, in like circumstances of concentration and of temperature, was acidified to the same extent, condensation started in one-fifteenth of the time required by a freshly-made mixture of carbamide and formaldehyde (Expt. 15). Dimethylol-carbamide, on the other hand, is relatively slow to condense—a fact already noted by Einhorn and Hamburger (*loc. cit.*). The reason, no doubt, is that the dimethylol derivative of 'methylenecarb-amide' (IV, above) resists formation in the presence of acids; so that, until time enough has passed for the elimination of a certain amount of formaldehyde, condensation is barred. No doubt, too, the complete stoppage of the carbamide–formaldehyde condensation (see above) by a very large excess of formaldehyde is due to the maintenance of the carbamide in the state of its dimethylol deriv-ative; if the uncondensable mixture is added to a concentrated aqueous solution of carbamide, a precipitate separates forthwith (Expt. 9).

Having regard to the above facts, one may reasonably judge that " methylenecarbamide " results from the decomposition of · some compound, generated by the action of, say, hydrochloric acid on methylolcarbamide. Of the stages that must occur, the first is probably the change of $NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot OH$ into

$$NH_2 \cdot CO \cdot NH \cdot CH_2Cl,$$
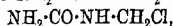
a compound, likely to be unstable, owing to the loss (at least, if water is present) of hydrogen chloride. Through the elimination of hydrogen chloride there originates the residue, $\cdot NH \cdot CO \cdot NH \cdot CH_2 \cdot$, whence, by polymerisation, the compound $CO{<}^{NH \cdot CH_2 \cdot NH}_{NH \cdot CH_2 \cdot NH}{>}CO$ (" methylenecarbamide ") could occur. An essentially similar change, in fact, has been observed by Chattaway (T., 1909, **95**, 236), chlorocarbamide, by the loss of hydrogen chloride, polymeris-ing thus:

$$CO{<}^{\cdot NH_2}_{NHCl} + CO{<}^{NHCl}_{NH_2} \rightarrow 2HCl + CO{<}^{NH \cdot NH}_{NH \cdot NH}{>}CO.$$
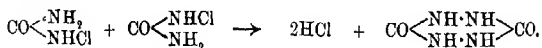
Really, however, the carbamide–formaldehyde process is some-what more complex than is here indicated, for, as previously men-tioned, molecular proportions of carbamide and formaldehyde do not give pure " methylenecarbamide "; moreover, the condensate of a tolerably pure specimen of methylolcarbamide was markedly con-taminated with a substance poorer in nitrogen. Further inquiry

showed that, in the acid condensation of methylolcarbamide, a secondary reaction occurs, the compound being decomposed, to some extent, into carbamide and formaldehyde (a change like that of aldehyde–ammonia, except that the acid completely neutralises the ammonia, whereas it has but little power to fix a base so feeble as carbamide).

Now, an aqueous solution of methylolcarbamide gives, with sodium nitroprusside and phenylhydrazine, no reaction for formaldehyde, nor does it show the reaction for carbamide with mercuric nitrate; neither, when once formed, does "methylenecarbamide" unite with formaldehyde. As the last-named is produced immediately—that is, prior to condensation—the inference was that it must attack the nascent methylenecarbamide residues. If so, and if the proportion of formaldehyde is not sufficient to produce the incondensable dimethylol residues alone, one could foresee that methylolcarbamide, when condensed in the presence of a suitable amount of formaldehyde, should furnish Goldschmidt's compound. On experiment with molecular proportions of the two, this forecast was verified (Expt. 13).

As regards the condensation of carbamide with formaldehyde, a like mechanism is imaginable, since, even in the presence of an acid, the organic components might conceivably unite to form methylolcarbamide. With mixtures only slightly acidified, and hence condensing but slowly, this may be the case; on the other hand, with freely acidified mixtures, the condensation of which may happen within a few seconds, the action must run a different course. Experiment, in fact, has shown that condensation can be accomplished in circumstances where the existence of methylolcarbamide is precluded.

Thus, if carbamide (1 mol.) is dissolved in formalin (1 mol.) previously saturated with hydrogen chloride (and so changed into chloromethyl alcohol), no precipitate appears, a clear syrup being formed instead. If hydrogen chloride is passed through a molecular solution of carbamide in formalin until the clot which first separates dissolves again, a clear syrup is formed, as before. Finally, if hydrogen chloride is led over moist, ready-formed "methylenecarbamide" (or if the latter is added to fuming hydrochloric acid), the solid disappears, giving place to a syrup. Each of these syrups, when poured into water, yields instantly a voluminous, white precipitate of the condensation product. On prolonged exposure in a vacuum over lime and over sulphuric acid, a clear, odourless, resinous material is left; deliquescent, evolving with cold sulphuric acid fumes of hydrogen chloride, and decomposed at once by water, the whole of the contained halogen passing

L* 2

into solution as hydrochloric acid, whilst a condensation product
is deposited.

These changes, perhaps, may be represented by the equations:

(a) $CO(NH_2)_2 + CH_2Cl \cdot OH \longrightarrow H_2O + NH_2 \cdot CO \cdot NH \cdot CH_2Cl$,

(b) $CO {<}^{NH}_{NH}{>} CH_2 + HCl \longrightarrow NH_2 \cdot CO \cdot NH \cdot CH_2Cl$,
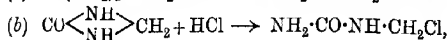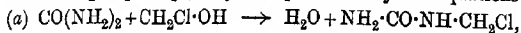
the product, with excess of water, decomposing as earlier suggested
(in the latter equation, for simplicity, the halved formula is used
for "methylenecarbamide"). The substances, however, were not
pure, nor, by reason of their deliquescence and instability, could
any method be devised for their purification.

The possibility that water, in removing the elements of hydrogen
chloride, might produce methylolcarbamide (which, of course,
would react with the liberated acid), was negatived by the observa-
tion that the change occurred equally when the material was added
to dilute alkali hydroxide or to a solution of ammonia.   Had
methylolcarbamide thus been formed, the acid simultaneously
being neutralised, no immediate condensation would have followed;
although not decisive, these results are consistent with the view
already suggested, namely, that "methylenecarbamide" originates
from a residue, $\cdot NH \cdot CO \cdot NH \cdot CH_2 \cdot$, derived from the compound,
$NH_2 \cdot CO \cdot NH \cdot CH_2Cl$, or from one of its congeners; that is, in the
acid process, with which alone the present paper is concerned.

Dimethylolcarbamide may be produced by evaporating a neutral
solution of carbamide in a sufficiency of formalin and crystallising
the solid residue from alcohol. The fused material soon decom-
poses into water, formaldehyde and Goldschmidt's compound,
$C_5H_{10}O_3N_4$, an aqueous solution, when acidified, behaving in the
same way.

From random acidified mixtures of carbamide and formalde-
hyde, $C_5H_{10}O_3N_4$ is the product likely to preponderate.   The
result, however, depends on the conditions imposed; and that
different workers, handling these ill-defined, amorphous, insoluble,
and generally similar materials should have disagreed, more or
less, as to the outcome, is not surprising. In the present research,
the results to some extent have been disentangled; it is almost
certain, however, that the condensation of carbamide with form-
aldehyde is a reaction more complex than has been indicated above,
both as regards the mechanism and the composition of the pro-
ducts of condensation. It need scarcely be added that, in these
reactions, hydrochloric acid is no more a catalyst than is the water
or the carbamide or the formaldehyde.

Any definite acid that does not itself decompose carbamide may
accomplish the foregoing condensations, either with mixtures of

carbamide and formaldehyde or with the methylolcarbamides, but, of the products obtained with nearly a dozen different acids, no quantitative analyses were made. Carbonic acid was the weakest tried; at the ordinary temperature and under the pressure of one atmosphere, a solution of one molecular proportion of carbamide in one of formalin, previously neutralised, remained clear for two or three days, but gave ultimately a dense precipitate. None of the pure condensation products when kept for an hour in contact with water and urease gave a detectable quantity of ammonia.

EXPERIMENTAL.

Unless it is otherwise stated, the "formaldehyde" used in the experiments described below was commercial formalin containing 37·5 grams of formaldehyde in 100 c.c. of the solution.

Expt. 1.—To 6 grams of carbamide in 100 c.c. of water (free from air), 9 c.c. of formalin were added; the mixture, neutralised with dilute sodium hydroxide and sealed up from contact with the external air, remained clear during six months, at the end of which period the experiment was stopped. Portions removed from time to time and acidified with hydrochloric acid or with sulphuric acid became densely turbid within a few seconds.

Expt. 2.—Without the preliminary neutralisation, Expt. 1 was repeated; in four hours, opalescence was visible, and next day a copious precipitate had separated.

Expt. 3.—Expt. 2 was repeated, 2 c.c. of formic acid solution being added to the mixture, which became turbid in less than half an hour. Next day, the precipitate was removed, washed with boiling water, and dried; its weight amounted to 0·91 of that possible for $C_4H_8O_2N_4$. The product consisted of minute, nearly spherical granules showing in plane-polarised light a black cross, and decomposing with effervescence and browning at about 242° (uncorr.) (in another experiment, at 239°). With rapid heating, the temperature of decomposition may rise by at least 10°. (Found: $N = 38\cdot3$; $C_4H_8O_2N_4$ requires $N = 38\cdot89$ per cent.)

When the carbamide–formaldehyde ratio was exactly 1:1, the percentage of nitrogen in the condensation product was 38·4, the same result also being obtained when a solution containing only 2 per cent. of carbamide was condensed; in both cases, hydrochloric acid was the catalyst used.

Expt. 4.—Carbamide (1 mol.) in tepid aqueous solution and formaldehyde (0·7 mol.), when condensed with hydrochloric acid, yielded a product similar to the preceding, but giving $N = 38\cdot9$ per cent.

A quantity kept for twenty-four hours in contact with a large excess of formalin and then analysed contained about 1 per cent. of nitrogen less than before; hence the ready-formed material does not unite with formaldehyde to produce Goldschmidt's compound ($N = 32\cdot18$ per cent.). The slight diminution in the nitrogen-content is probably due to the presence of a little paraformaldehyde, an insoluble, gelatinous material, which tends to separate from formaldehyde solutions when acidified and exposed to the air. Always, in fact, when the condensing mixtures contain free form-aldehyde, a skin of this substance appears on the surface, and has to be removed; but, even so, the nitrogen-content is often a fraction of a per cent. below the calculated value.

Expt. 5.—A solution of carbamide (1 mol.) in its own weight of water, slightly warmed and mixed with formaldehyde (1·5 mols.), was condensed with hydrochloric acid. Time, three seconds; yield, 0·87 of that calculated for $C_5H_{10}O_3N_4$. (Found: $N = 31\cdot7$; $C_5H_{10}O_3N_4$ requires $N = 32\cdot18$ per cent.)

Notwithstanding the large diminution in the percentage of nitrogen, the properties and reactions were much the same as those of "methylenecarbamide." The substance was decomposed by boiling, dilute mineral acids into carbamide and formaldehyde; it was insoluble in all the common solvents; the granules showed in plane-polarised light and under a magnification of 600 diameters the black cross exhibited by the compound mentioned.

Expt. 6.—Carbamide (1 mol.), dissolved in formaldehyde (2 mols.) at the ordinary temperature, was condensed with hydro-chloric acid. Time, fifteen seconds (five seconds when the mixture was kept for one and a-half hours previously to acidification); yield, about the same as in the last experiment. Properties, similar; decomposing point, 244°, or with rapid heating 254° (uncorr.). (Found: $N = 31\cdot6$; $C_5H_{10}O_3N_4$ requires $N = 32\cdot18$ per cent.)

Expt. 7.—Expt. 6 was repeated with formic acid as "catalyst," a little water being added later to prevent dense solidification. Time, about two minutes; yield, 0·75 of the calculated; decom-posing point, with moderately slow heating, 240°. (Found: $N = 32\cdot1$; $C_5H_{10}O_3N_4$ requires $N = 32\cdot18$ per cent.)

After five days' contact with formalin in excess, found $N = 32\cdot2$ per cent.; no combination, therefore, had occurred.

Expt. 8.—Carbamide (1 mol.) in formaldehyde (4 mols.) gave with hydrochloric acid a slight turbidity, not increased by dilution with water. Very slowly, the deposit thickened, and after twenty-four hours was removed; its weight was but 0·35 of that (4·5 grams) of the carbamide employed. The decomposing point was

a shade lower than in the preceding cases (about 233° when put into the apparatus at 150° and 243° when put in at 205°); otherwise, the substance had the properties already described. (Found: $N = 29\cdot3$; $C_5H_{12}O_4N_4$ requires $N = 29\cdot17$ per cent.)

This material appears to contain 1 mol. of water more than the compound, $C_5H_{10}O_3N_4$, obtained with a smaller amount of formaldehyde. The experiment was repeated, the mixture being allowed to remain for an hour before treatment with the acid; no difference, however, was noticeable in any way, except that, after forty-eight hours, the yield was 0·48 of the weight of carbamide taken, and that some flakes of paraformaldehyde were present. By sifting, these were removed and the nitrogen was estimated; it was almost the same as before, namely, 29·1 per cent. Possibly, the compound has the structure represented by the formula $NH_2\cdot CO\cdot N(CH_2\cdot OH)\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot OH$, or the methylol groups may be attached to the terminal nitrogen atoms.

Expt. 9.—With 11 mols. of formaldehyde to 1 mol. of carbamide, although the temperature rose perceptibly on the addition of the acid (hydrochloric), the mixture remained clear. Dilution with water or treatment with more acid had no effect, but after a few days' exposure in an open vessel, some paraformaldehyde began to separate. When the clear liquid was poured into a concentrated solution of carbamide, a condensation product rapidly appeared, of which no analysis was made.

In all the preceding experiments, the amount of hydrochloric acid used was roughly 1 c.c. of the concentrated acid (D 1·16) per 6 grams of carbamide; with much larger proportions of acid, the results were as stated below.

Expt. 10.—Two grams of carbamide, in each case, were dissolved in fuming hydrochloric acid: (i) 1 c.c.; (ii) 2 c.c.; (iii) 3 c.c.; (iv) 4 c.c.; (v) 6 c.c. Then, to each of the first four solutions were added 2·5 c.c. of formalin, diluted with the same acid to 4 c.c.; to the fifth, 3 c.c. of formalin; the respective temperatures attained were 55°, 55°, 52°, 48°, and 44°. Soon, (i) became opaque and solidified; (ii), on cooling, changed to a silica-like jelly; (iii) developed presently a few small clots, which later redissolved; (iv) and (v) remained permanently clear; all the solutions, when diluted with water, forthwith became thickly turbid. After remaining for ten days in a vacuum over lime and sulphuric acid respectively, (iv) formed a stiff, almost solid syrup, giving up to water HCl = 23·5 per cent. of its weight.

Expt. 11.—Hydrogen chloride was passed through a cooled solution of carbamide in 1· molecular proportion of formaldehyde, and the resultant clear, viscous syrup poured off from the clot of con-

densation product. In a vacuum, as before, the syrup, after several weeks, changed to a resin, which decomposed instantly with water, giving up to the latter, $HCl = 25.4$ per cent. On exposure to the air, the resin first deliquesced, yielding a clear, mobile liquid; as more moisture was absorbed, this became turbid, and finally solidified, owing to the separation of a condensation product. The experiment was repeated, the gas being passed until all the clot had redissolved; the syrup, treated as before, gave a clear resin having the properties described above, and yielding to water $HCl = 24.5$ per cent.

Expt. 12.—Dry hydrogen chloride had no visible effect on dry "methylenecarbamide," but when the latter was moistened and the passage of the gas continued, the solid gave place to a colour-less syrup, gradually hardening in a vacuum. To water, the solid product gave up $HCl = 27.3$ per cent., a condensate separating, in which was found $N = 37.85$ per cent. (the sample of "methylene-carbamide" taken for experiment contained $N = 38.0$ per cent.). When added to dilute alkali hydroxide or to a solution of ammonia, the chloro-derivative behaved exactly as towards water, hydrogen chloride being eliminated and neutralised by the excess of alkali present, whilst a condensation product was instantly deposited.

Like results were obtained when carbamide was dissolved in formalin, previously saturated with hydrogen chloride (or mixed with excess of fuming hydrochloric acid), and when "methylene-carbamide" was dissolved in cold, fuming hydrochloric acid, the product in all cases being a syrup, behaving as described above. From the foregoing results, it is evident that carbamide, form-aldehyde, hydrogen chloride, and water together produce a balanced system, the equilibrium of which depends on the concentrations of the various components.

Solid carbamide hydrochloride, when exposed to the fumes obtained by rapidly distilling paraformaldehyde, did not appear to undergo any change.

Methylolcarbamide.

The somewhat elaborate procedure recommended by Einhorn and Hamburger (*loc. cit.*) for the preparation of this substance is un-necessary; by exposing for a day or two in an exhausted desiccator a solution of carbamide (1 mol.) in formalin (1 mol.), just neutralised by dilute alkali hydroxide, a viscid, crystalline paste was obtained, from which, after a couple of recrystallisations from alcohol, methylolcarbamide was isolated in brilliant, flattened prisms melting at about 110° (corr.). (Found: $N = 30.9$; $C_2H_6O_2N_2$ requires $N = 31.11$ per cent.).

The aqueous solution was odourless, and gave with sodium nitro-prusside and phenylhydrazine no reaction for formaldehyde, and with neutral mercuric nitrate no reaction for carbamide. On acidification, however, formaldehyde was detected, both prior to condensation and long after the process appeared to be complete.

Dimethylolcarbamide.

A neutralised solution of carbamide (1 mol.) in a little more than 2 mols. of formalin, when treated as above, yielded dimethylol-carbamide; it had essentially the properties described by Einhorn and Hamburger, including the relatively slow condensation by acids. In moderately concentrated solutions, this process requires approximately minutes, where seconds are needed in the case of the monomethylol analogue. Otherwise, its behaviour in an aqueous solution was the same as that of methylolcarbamide.

The fused material soon began to decompose (m. p. about 123°), water and formaldehyde escaping, and a white, amorphous solid being left; this, when heated alongside a pure specimen of the compound, $C_5H_{10}O_3N_4$, melted at the same moment as the latter, and with similar effervescence and browning (255°, uncorr.; both introduced into the bath at 235°). By condensing an aqueous solution with dilute hydrochloric acid, the same product was obtained as by heating; it gave $N = 32.8$ per cent., whereas $C_5H_{10}O_3N_4$ requires $N = 32.18$ per cent. The end result of these changes may thus be represented:

$$2CO(NH \cdot CH_2 \cdot OH)_2 \longrightarrow H_2O + CH_2O + C_5H_{10}O_3N_4.$$
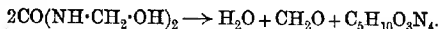
Expt. 13.—Approximately pure methylolcarbamide, when condensed by means of dilute hydrochloric acid, yielded a product containing only 35.5 per cent. of nitrogen ("methylenecarbamide" requires $N = 38.89$ per cent.), the deficit presumably being due, as earlier suggested, to the attack of the methylolcarbamide, when in the act of yielding its normal condensation product, by the form-aldehyde which is liberated before that act is complete.

The experiment was repeated, 1 molecular proportion of form-aldehyde being first added to the solution of methylolcarbamide; in these circumstances, the solid product was found to consist solely of Goldschmidt's compound. (Found, $N = 32.25$. $C_5H_{10}O_3N_4$ requires $N = 32.18$ per cent.)

Expt. 14.—In order to learn whether the last-named compound might result through an interaction between the two methylol-carbamides, somewhat as follows:

$$NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot OH + CO(NH \cdot CH_2 \cdot OH)_2 \longrightarrow$$
$$2H_2O + C_5H_{10}O_3N_4,$$
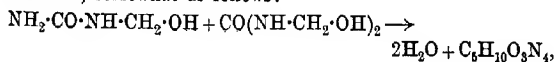
a molecular mixture of the components, in aqueous solution, was acidified, the mixture (which began to condense in forty seconds) being allowed to remain overnight. Here, if the two jointly condensed, the sole product must be the material containing $N = 32.18$ per cent., whereas, if they condensed independently, the first precipitate would be the mixture referred to in Expt. 13 as containing $N = 35.5$ per cent., to which later the condensate of dimethylolcarbamide ($N = 32.18$ per cent.) would add itself; so that, ultimately, the product must give a figure somewhere between the two. The percentage actually found was 33.35, and when the experiment was repeated, but with 0.75 mol. of dimethylolcarbamide, the figure was 34.6; hence, it is concluded that, in a mixture of methylol- and dimethylol-carbamide, acidified with hydrochloric acid, the two substances condense independently.

Although in the acid condensation of the former, the elimination of formaldehyde prevents the production of pure "methylenecarbamide," yet fused methylolcarbamide soon decomposes, water being evolved, but little or no formaldehyde. In this case, the residue is doubtless free from much contamination with Goldschmidt's compound; no analysis, however, was made.

Expt. 15.—Solutions were prepared (*a*) of methylolcarbamide, (*b*) and (*c*) of carbamide and formaldehyde in molecular proportion. All had the same "carbamide-concentration" (1 gram in 6 c.c.); equal volumes of each, at 13°, were acidified with one-twelfth the volume of concentrated hydrochloric acid. Prior to acidification, however, (*b*) was kept at 13° for an hour and a half. The times elapsing before precipitation were, for (*a*) less than three seconds, for (*b*) twenty-eight seconds, for (*c*) forty-five seconds. Ready-made methylolcarbamide, therefore, condensed at least fifteen times as rapidly as a mixture of its components, which had remained for some five or six minutes, whilst a like mixture, kept beforehand for an hour and a-half, condensed in nearly half the time.

Evidently, the union of formaldehyde with carbamide takes place only by degrees; in fact, a solution, kept for twenty-four hours in a vacuum desiccator, still had a strong odour of formaldehyde. In the presence of barium hydroxide, too, at the concentration recommended by Einhorn and Hamburger, the same phenomenon was noticed.

CHEMISTRY DEPARTMENT,
    UNIVERSITY COLLEGE,
        CORK.

XXIX.—*The Sub-bromide and Sub-chloride of Lead.*

By HENRY GEORGE DENHAM.

IN a recent paper (T., 1917, **111**, 29), the author has described a method for the preparation of lead sub-iodide by the action of methyl iodide vapour on lead sub-oxide. As indicated in that paper, the method appears of a somewhat general nature, applicable at least to the preparation of other sub-salts of lead. In the present paper, the method has been used to prepare lead sub-bromide and sub-chloride, the only radical alteration being in the replacement of the methyl haloid by the ethyl compound, owing to the more convenient boiling point of the higher homologue.

Lead Sub-bromide.

The apparatus already described in the previous paper (*loc. cit.*) has, with a few minor alterations, proved quite suitable. The lead sub-oxide was prepared from lead oxalate (Found: $Pb = 70\cdot17$. Calc.: $Pb = 70\cdot18$ per cent.) precipitated from an acid solution of lead acetate by the addition of oxalic acid, the actual decomposition of the oxalate into the sub-oxide being carried out precisely as described in the former paper. The alterations in the apparatus to be noted were the replacement of phosphoric oxide as a drying agent by anhydrous calcium chloride, and the introduction of a contriction in the glass tubing leading from the oven to the condenser. The former was a matter of necessity, owing to a temporary shortage of the phosphoric oxide, the latter was devised to facilitate the control of the distillation. Shortly after the ethyl bromide[*] had been introduced into the apparatus, a little distillate collected at the constriction and formed a most convenient gauge for noting the velocity of distillation. This is a very

---

[*] *Purification of the Ethyl Bromide.*—The ethyl bromide was prepared from chemically pure potassium bromide, ethyl alcohol, and sulphuric acid. The distillate was treated with dilute sodium carbonate solution, several times with water, then shaken at least four or five times with concentrated sulphuric acid, and finally with water (owing to a tendency to emulsify, it was often found necessary to wash several times with dilute sodium hydroxide solution before the final washing with water). The bromide was dried over calcium chloride, and fractionated from phosphoric oxide, the fraction of constant boiling point alone being used. This method of purification had to be rigidly followed, otherwise samples of ethyl bromide were obtained that contained traces of some reactive impurity in sufficient quantity to cause appreciable errors when a relatively large amount of the bromide was distilled through the sub-oxide.

essential point, for the ethyl bromide appears to react much less vigorously with lead sub-oxide than does methyl iodide. Thus, in the preparation of lead sub-iodide, about fifty minutes' distillation sufficed to convert the sub-oxide into the sub-haloid, whilst in the present case at least 150 minutes' distillation was required to secure complete reaction. The need for a preliminary heating of the vapour before it enters the reaction bulb is even more necessary than in the case of lead sub-iodide. This was again obtained by passing the vapour through a capillary spiral. The extreme slowness of the reaction naturally leads one to search closely for the temperature at which the ethyl bromide just escaped decomposition. By the process of "bracketing," it was found that the distillation can be safely carried through at 261°, but not higher. At temperatures much lower than this, the last traces of sub-oxide react very sluggishly; for example, at 258°; analysis indicated the presence of 74·1 per cent. of lead (PbBr requires $Pb = 72·16$ per cent.), although, by the prolonged absence of the evolution of gas, the reaction appeared quite complete. At 262° gas was evolved until the end of the experiment, the product was much lighter than that obtained in experiments carried out at 261°, and analysis gave $Pb = 70·2$ per cent. Undoubtedly there had been incipient decomposition of the bromide vapour, with liberation of bromine and subsequent oxidation of the lead sub-bromide to the normal bromide. Indeed, it may be safely asserted that whenever this evolution of gas continues throughout the experiment, one invariably obtains a product contaminated by more or less lead bromide. After the distillation was completed, the receiver containing the distillate was cooled with liquid ammonia, the apparatus partly exhausted, the receiver sealed off, and the exhaustion continued until the pressure had fallen to about 1 mm. It was found to be unnecessary to continue the exhaustion longer as several experiments showed no trace of a volatile product, such as occurred in the preparation of lead subiodide. On the other hand, the amount of non-volatile carbonaceous matter was sufficiently high to necessitate estimation, generally amounting to from 0·3 to 0·5 per cent. of the weight of the lead sub-bromide.

Method of Analysis.—The mixture of lead sub-bromide, carbonaceous matter, and silica was digested with concentrated acetic acid, then extracted with water; after four extractions the residue was treated with a little hot, very dilute nitric acid, as it was found that the carbonaceous matter otherwise tended to coagulate and retain traces of lead bromide. Two washings with the dilute nitric acid sufficed to remove the whole of the dissolved bromide. The

bromine was then weighed as silver bromide; the silica and carbon were weighed in a Gooch crucible, and after ignition in a muffle the weight of carbon was obtained by difference.

The analytical details of the accompanying experiment will make clear the use to which the knowledge of the percentage of carbon was put in arriving at the percentage of lead in the sample.

Typical Experiment.

Two bulbs each containing about 5 grams of lead oxalate intimately mixed with 2 to 3 grams of powdered silica.

Decomposition took place at a maximum temperature of 340° and maximum pressure of 5 cm. Ethyl bromide: about 15 c.c. Temperature of distillation, 261°. *Remarks.*—Five c.c. of distillate had collected in sixty-five minutes. No gas evolution for the last forty minutes. Duration of distillation, one hundred and thirty-five minutes.

Estimation of Lead :—

Weight of bulb and contents	=	8·6648
,, ,, ,, ...	=	3·7758
,, ,, carbon, silica, bromide	=	4·8890
Corrected for air displacement	=	4·8910
Weight of silica	=	4·4039
,, ,, carbon (calculated from Br analysis)	=	0·0017
,, ,, bromide used....................;...............	=	0·4854
,, ,, lead sulphate.......................................	=	0·5148
Percentage of Pb	=	72·40

Estimation of Bromine :—

Weight of bulb and contents	=	8·6020
,, ,, ,, ...	=	3·4394
,, ,, carbon, silica, bromide	=	5·1626
Corrected for air displacement	=	5·1644
,, carbon and silica	=	4·4927
,, substance	=	0·6717
,, AgBr found	=	0·4424
Percentage of Br..·.............	−	28·03

Synopsis of Results.

Experiment.	Duration of distillation.	Absence of gas evolution for	Pb. Per cent.	Br. Per cent.
1	135 min.	40 min.	72·5	28·0
2	122 ,,	20 ,,	71·7	28·4
3	140 ,,	25 ,,	71·6	27·5
4	180 ,,	60 ,,	72·5	27·3
5	180 ,,	20 ,,	72·5	28·4
6	175 ,,	20 ,,	71·7	28·2
7	135 ,,	50 ,,	71·8	28·0
8	135 ,,	65 ,,	72·6	28·0
9	155 ,.	90 ,,	71·9	27·9
		Mean	72·09	27·97
		Calc.	72·16	27·84

The slight fluctuations about the mean undoubtedly arise from the extreme difficulty in (a) securing complete absence of oxygen, not only in preparing the sub-oxide, but in the introduction of the ethyl bromide and in the distillation, for example, 0·1 c.c. of oxygen let into the apparatus would cause an error of nearly 0·2 per cent. in the estimation of bromine; (b) maintaining the temperature of the oven just below that of incipient decomposition during distillation; and (c) securing sufficiently slow velocity of distillation to secure thorough heating of the vapour throughout a lengthy experiment.

Properties of Lead Sub-bromide.—The substance oxidises very slowly, more rapidly if the air is moist. After boiling with water in the air and filtering, very little evidence is obtained in the filtrate either of lead or of bromine, whilst if a saturated solution of the sub-bromide is prepared in the absence of air, there is obtained with hydrogen sulphide a darkening in the colour of the solution, but no precipitate separates; under similar conditions lead bromide gives a heavy, black precipitate. A saturated solution prepared in a vacuum gives with silver nitrate only a faint opalescence.

The colour of the sub-bromide appears to be a distinct gray, and although the presence of 0·3 to 0·5 per cent. of carbonaceous matter must necessarily darken the colour, there is little doubt that the grayish appearance is characteristic of the sub-bromide for the following reasons: (a) Whenever analysis gives a higher percentage of bromine than 27·9, that is, whenever oxidation has occurred through the temperature being sufficiently high to liberate bromine from the ethyl bromide with consequent oxidation of the sub-bromide to the normal bromide, the colour changes to a much paler one, the substance becoming at times nearly white.

After a rapid distillation carried out at 300° the product was found to be a pale gray, although the percentage of bromine did not exceed 30·6.

Moreover, such a pale coloured product gives, on extraction with hot water, a copious precipitate with a solution of silver nitrate, a reaction which totally fails when the gray product is used.

(b) On heating gray lead sub-bromide in a vacuum for two hours at 370°, the colour becomes distinctly paler, and a rapid extraction with hot water reveals the presence of a considerable amount of lead bromide.

The sub-bromide slowly decolorises bromine water, rapidly on warming to about 50°. The sub-bromide, on treatment with acetic acid, nitric acid, etc., immediately decomposes into lead and lead bromide, and after diluting and boiling, complete solution takes place, except for a small quantity of carbonaceous matter.

Determination of Solubility.—As a further proof of the individuality of the compound, the determination of the solubility of the salt in a vacuum by the conductivity method was used. The apparatus already figured (*loc. cit.*) was again used. Small bulbs of thin glass containing silica and about 0·1 gram of lead sub-bromide were prepared by the usual method, and the purity of the samples was controlled by the analysis of the contents of larger bulbs. The actual procedure already described (*loc. cit.*) was closely followed.

The resistance of a saturated solution of carefully prepared lead bromide at 25° was found to be 22 ohms, remaining constant for two hours.

The mean of two closely agreeing experiments with lead sub-bromide gave the following results:

Resistance of the water before breaking the bulb...... = 26000 ohms.
After breaking the bulb...................................... = 1860 „

this remaining unchanged for several hours.

If the ionic mobilities of the bromine and the lead ions (whether Pb^+ or Pb_2^{++}) are assumed to be the same as in the case of the normal bromide (76·6 and 71·8 respectively), and if complete dissociation takes place, the solubility of the sub-bromide is 0·4 milli-equivalent per litre. This value is about the same as that for the subiodide already recorded (0·35 milli-equivalent per litre), but in both cases it must be emphasised that the values obtained for the solubility are probably a little high, due to unavoidable traces of the normal salt. Such traces are almost certain to be formed through the action of heat on the sub-salt during the sealing of the bulb, whilst the carbonaceous matter, too, may exert an influence on the solubility.

Lead Sub-chloride.

When the lead oxalate has been completely decomposed into sub-oxide about 10 grams of ethyl chloride thoroughly cooled by liquid ammonia were introduced into the distillation flask. By this means any desired quantity could be rapidly introduced from the tubes. The distillation of the chloride could be rapidly regulated by adjusting the temperature of the water-bath, but owing to the low boiling point of the chloride no effort was made to collect the distillate. The reaction between the sub-oxide and the vapour of the ethyl chloride was very slow, and it was soon found that approximately three hours were required for the distillation and a temperature as high as 311° (as recorded by a standardised thermometer). This is shown in the following table.

TABLE I.

Experiment.	Temperature.	Duration.	Cl. Per cent.
1	261°	85 min.	4·2
2	275	135 ,,	7·4
3	300	165 ,,	11·1
4	310–11	165 ,,	14·4
5	312	160 ,,	15·0
6	315	180 ,,	17·2
		Theoretical ...	14·ᐤ

The highest temperature at which the distillation may be carried out appears to be 311°, and the duration of the experiment in the neighbourhood of three hours. The slowness of reaction suggested that it might be possible to carry through the experiment without having silica present, as was the case with the sub-iodide. In two experiments it was impossible to detect any difference between samples prepared in the presence and in the absence of silica, and in the majority of the experiments tabulated in table II silica was not used as diluent. The only other change in the procedure was that phosphoric oxide was again used as a drying agent, in order to eliminate any traces of ammonia absorbed by the ethyl chloride when it was being introduced into the apparatus.

Method of Analysis.—A slight modification in the method of estimating lead was necessary owing to the high percentage of carbonaceous matter retained in the reaction bulbs. As a rule the estimation of chlorine revealed the presence of about 2 per cent. by weight of carbonaceous matter. The low value at first found by the old method in the estimation of lead under conditions when the estimation of chlorine led one to expect that a pure

sample of sub-chloride had been obtained, suggested that this carbonaceous matter, impregnated as it would be with lead sulphate, might be exercising a reducing action with a consequent slight loss of lead. Thus in one experiment the percentage of chlorine found was exactly correct, whilst the percentage of lead was 84·4 (calc., 85·4). Two bulbs were then prepared, the lead in one being estimated by the method already described; in the other the sub-chloride was extracted five times with hot dilute nitric acid, the filtrate concentrated in a weighed silica crucible, and finally evaporated with excess of sulphuric acid. The results by the old and the new methods were respectively 83·6 and 85·1 per cent., a duplicate experiment giving identical results. The results recorded in table II were obtained by the modified method for estimating lead, the percentage of chlorine being obtained in a manner similar to that described for the bromide, except that no estimation of silica was necessary.

The analytical results are given in table II.

TABLE II.

Experiment.	Duration of distillation.	Pb. Per cent.	Cl. Per cent.
10	190 min.	85·14	14·24
11	205 ,,	85·30	14·85
12	165 ,,	85·53	14·90
13	210 ,,	85·11	14·60
14	210 ,,	85·17	14·04
15	180 ,,	85·94	14·91
	Mean	85·36	14·59]
	Theoretical ...	85·39	14·61

Properties of Lead Sub-chloride.—The colour of the sub-chloride is closely similar to the gray colour of the sub-bromide. It must again be emphasised that the gray appearance does not arise from the presence of the carbonaceous matter, for if the sub-chloride is heated in a vacuum above 400°, it becomes nearly white owing to the reaction:

$$2PbCl \longrightarrow PbCl_2 + Pb,$$
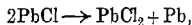
the whiteness of the normal chloride more than compensating for the darkness arising from the presence of an equivalent quantity of lead. The sub-chloride is fairly stable in air, but rapidly decolorises bromine water and permanganate solution.

A saturated aqueous solution of lead sub-chloride prepared in a vacuum gives a faint precipitate with silver nitrate as well as with hydrogen sulphide, strongly contrasting in this respect with

the less readily soluble sub-bromide and sub-iodide. The sub-salt is also readily decomposed by acids.

Determination of Solubility.—As a quantitative proof that the gray substance is not an intimate mixture of lead and lead chloride in molecular quantities, a comparison of its solubility with that of the normal chloride has been made by the conductivity method already described.

Resistance of a solution of lead chloride, three times recrystallised, at $25° = 15·9$ ohms, a second determination giving the same result.

A small bulb containing 0·1 gram of lead sub-chloride was broken in a vacuum.

Resistance before the bulb was broken .... $=$ 21000 ohms.
    ,, after ,, ,, ,, ,, ... $=$ 340 ,,

If one assumes the ionic mobilities of the lead and chlorine ions to be the same as for the normal chloride (71·8 and 75·5 respectively) and that complete dissociation takes place (highly probable if the constitution of the salt is represented by the formula $PbCl$, but subject to correction if the formula should prove to be Pb_2Cl_2), the solubility is found to be 2·2 milli-equivalents per litre.

Summary.

1. Lead sub-chloride and lead sub-bromide have been prepared by the action of ethyl chloride or bromide vapour at 311° and 261° respectively on lead sub-oxide.

2. Both compounds are grey, sparingly soluble, fairly stable in air, but readily oxidised by bromine water.

3. The sub-chloride has a solubility of about 2·2 milli-equivalents per litre, the sub-bromide 0·4 milli-equivalent per litre.

4. The sub-salts are readily decomposed by acid into the normal salt and metal.

CHEMICAL LABORATORY,
   UNIVERSITY OF QUEENSLAND,
      BRISBANE.

XXX.—*The Structure of Crystalline β-Methylfructoside.*

By ETTIE STEWART STEELE.

CONSIDERING the part played by fructose as a constituent of natural disaccharides and polysaccharides, the simple condensation reactions of the sugar are invested with a special importance. The prosecution of these studies is, however, seriously handicapped by the fact that few crystalline compounds are known to result from such condensations, and further complication is introduced by the recent observation that fructose may react in two forms, one of which is constituted according to the ethylene–oxide type of sugar (Irvine and Robertson, T., 1916, **109**, 1305).

Taking these factors into account, it is evident that the examination of the formation of fructosides is beset with difficulties. Thus, the action of acid methyl alcohol on fructose leads to the production of an uncrystallisable syrup, which Fischer (*Ber.*, 1895, **28**, 1145) originally regarded as essentially methylfructoside, and that this product was a mixture of isomeric fructosides was afterwards shown by Purdie and Paul (T., 1907, **91**, 289), who traced the progress of the condensation by polarimetric observations. The complexity of the reaction between fructose and methyl alcohol was further indicated by the fact that, on methylation followed by hydrolysis, the above mixture of fructosides gave rise to two distinct forms of tetramethyl fructose, one of which is crystalline and the other a colourless syrup. The optical relationships of the solid variety of tetramethyl fructose corresponded with those which might reasonably be expected on the assumption that, during the formation of methylfructoside, the parent sugar had reacted partly in the normal butylene–oxide form, and that this structure was preserved in the alkylated ketose. On the other hand, the nature of the syrupy isomeride remained obscure until it was recognised that fructose, in common with other reducing sugars, is capable of reacting in an entirely different form, containing presumably the ethylene–oxide linking. These views have already received expression (Irvine and Robertson, *loc. cit.*), and the explanation has been put forward that the syrupy methylfructoside described by Fischer contains four isomeric compounds, two of which are derived from the normal and two from the abnormal forms of the parent sugar.

The isolation by Hudson (*J. Amer. Chem. Soc.*, 1916, **38**, 1216) of a definite crystalline variety of methylfructoside presents an opportunity to test these views and thus to correlate the results of

the different workers in this field. By ascertaining the behaviour of this pure solid fructoside towards potassium permanganate solution, it has now been shown that the compound belongs to the stable type, and thus corresponds with the ordinary a- or β-varieties of methylglucoside, and the magnitude of the specific rotation of the compound is in agreement with this view. With this point settled, it has been possible to prove that the crystalline variety of tetramethyl fructose is likewise a derivative of the butylene-oxide form of fructose. The proof consists in the fact that Hudson's methylfructoside, on complete methylation and hydrolysis, is converted into a crystalline tetramethyl fructose identical with one of the products obtained by Purdie and Paul on subjecting syrupy methylfructoside to the same series of reactions.

It is thus possible to complete the interpretation of the somewhat complex reactions involved in the condensation of fructose with methyl alcohol. The sugar reacts in large measure in the ethylene-oxide form, giving rise to a highly reactive methylfructoside, but, at the same time, normal condensation takes place to a more limited extent. The condensation must thus resemble in many ways that involved in the formation of sucrose, as it has been shown that the fructose constituent of the disaccharide conforms to the ethylene-oxide sugar type (Haworth and Law, T., 1916, **109**, 1314). There is, in fact, an accumulation of evidence pointing to the idea that most fructose derivatives are constituted according to this plan, but, as already stated, a notable exception is provided by Hudson's crystalline methylfructoside and the tetra-acetyl fructose from which it is prepared, as these compounds are undoubtedly representatives of the stable butylene-oxide type.

The complete relationship between the reactions now correlated may be expressed in the scheme on page 259.

The definite compound A is thus a constituent of the mixture B, and is the source of crystalline tetramethyl fructose of the stable type.

Incidentally, in the course of the work a certain amount of fresh information has been gained as to the action of acetic anhydride and zinc chloride on fructose. Hudson's view that the reaction yields the tetra-acetate as an intermediate step in the formation of the penta-acetate has been supported. The yield of tetra-acetyl fructose is, however, only moderate even under the best conditions, and a considerable quantity of an uncrystallisable syrup is formed which has the composition of a triacetate. This was at first regarded as a mixture of partly acetylated fructoses, but as the composition and specific rotation were not altered by further action with acetic anhydride or by fractional treatment with solvents, it

Fructose

Mixture of
methylfructosides, *B*.

Tetra-acetyl fructose

Mixture of
tetramethyl methylfructosides

Tetra-acetyl ·
methylfructoside

Mixture of
tetramethyl fructoses

β-Methylfructoside, *A*.

Ethylene–oxide   Butylene–oxide
type (syrup)   type (crystalline).

Tetramethyl
β-methylfructoside.
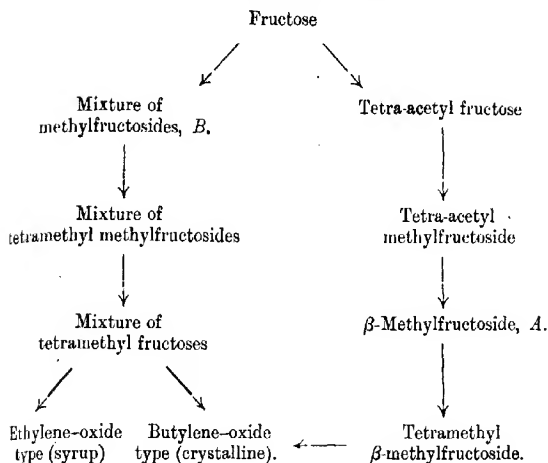
would appear to be a definite chemical individual. The compound showed the instantaneous reaction towards potassium permanganate solution which is characteristic of the ethylene–oxide type of sugars, and considering the special reactivity of such compounds, the resistance towards complete acetylation is remarkable. This steric hindrance also extends in some measure to alkylation, as, by treatment with silver oxide and methyl iodide, only one methyl group could be introduced into the compound, although two hydroxyl groups are presumably available for substitution.

In sharp contrast with these results, the crystalline tetra-acetyl fructose of the butylene–oxide type displays no resistance to complete substitution, as it can be readily converted into one variety of penta-acetyl fructose and also forms a fully acetylated methyl fructoside. In one respect, however, the compound is abnormal in that, although belonging to the butylene–oxide type and a true reducing sugar, it fails to display mutarotation. This has already been noted by Hudson, and is now confirmed in so far as repeated attempts to isolate the compound in mutarotatory forms invariably failed. In one sense, it is disappointing to find that tetra-acetyl fructose does not belong to the ethylene–oxide type, as the possibility seemed open that the compound might provide a suitable reagent for the synthesis of sucrose. The structural relationships of the compound, as now elucidated, are shown below, and, taken in conjunction with the constitutional study of sucrose contributed

by Haworth and Law (*loc. cit.*), render this expectation somewhat remote.

Fructose

(treated with acetic anhydride and zinc chloride reacts as) :—

Butylene-oxide fructose   Ethylene-oxide fructose

Tetra-acetyl fructose   Triacetyl fructose

Tetra-acetyl   Penta-acetyl   Further acetyl-   Methyl triacetyl
methylfructoside   fructose   ation arrested.   fructose

(No steric hindrance).

Further methyl-
ation arrested.
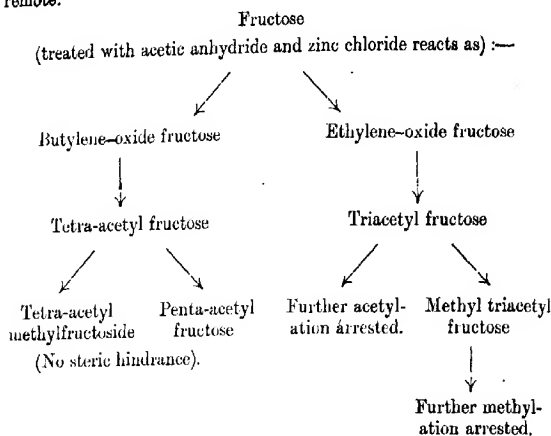
EXPERIMENTAL.

Preparation and Methylation of β-Methylfructoside.

The fructose employed was specially pure crystalline material prepared for bacteriological use by the hydrolysis of inulin. The sugar was converted into tetra-acetyl fructose in the usual way and thereafter methylated so as to produce tetra-acetyl β-methylfructoside. On removal of the acetyl groups by the agency of barium hydroxide, pure β-methylfructoside was obtained as described by Hudson (*J. Amer. Chem. Soc.*, 1916, **38**, 1216).

To a methyl-alcoholic solution of the fructoside (1 mol.) were added silver oxide (5 mols.) and methyl iodide (10 mols.) in the usual way, and the alkylation, which proceeded normally, was completed by six hours' warming on a water-bath. After filtration from silver iodide and extraction of the residue with boiling methyl alcohol, the solution was evaporated under diminished pressure to a syrup and the total product subjected to a second alkylation, in which the same proportion of the methylating agents was used. In this case no extraneous solvent was necessary as the syrup was freely soluble in methyl iodide. On isolation of the product, tetra-methyl β-methylfructoside was obtained as a colourless, mobile syrup, showing practically no action on Fehling's solution until after hydrolysis. The compound was identical with that obtained

by Purdie and Paul by condensing crystalline tetramethyl fructose with methyl alcohol by Fischer's method and the specific rotation displayed by the two preparations show little divergence.

Solvent: methyl alcohol; $c = 1.220$; $[a]_D - 120.1$.

Hydrolysis of Tetramethyl β-Methylfructoside.

A 3 per cent. solution of the methylated fructoside in 1.5 per cent. aqueous hydrochloric acid was hydrolysed by heating at 90° for thirty minutes. The solution was neutralised by means of barium carbonate, filtered, evaporated to dryness under diminished pressure, and the residue extracted with boiling ether. After drying and removal of the solvent, the syrup obtained in this way solidified completely to a mass of square plates. After two crystallisations from light petroleum the sugar melted at 92—95°, and showed downward mutarotation in the lævo sense, the permanent value being $[a]_D - 85.6$. The corresponding constants quoted by Purdie and Paul are m. p. 98—99° and $[a]_D - 86.7$. It is to be observed, however, that this maximum melting point refers to the pure stereoisomeride, and is thus attained only after repeated crystallisation. An average specimen of tetramethyl fructose melts in the neighbourhood of 95°, and the specimen now described showed no alteration in melting point when mixed with material prepared by Purdie and Paul. The composition of the sugar was confirmed by analysis. (Found, OMe = 50.65. $C_6H_8O_2(OMe)_4$ requires OMe = 52.54 per cent.)

Action of Acetic Anhydride and Zinc Chloride on Fructose.

Fifty grams (1 mol.) of pure crystalline fructose were added gradually to a solution of 4.5 grams of zinc chloride in 250 c.c. (10 mols.) of acetic anhydride and the mixture was stirred at 0° until the fructose had dissolved. The acetylated sugar was extracted with chloroform as described by Hudson, whereby 45 grams of crystalline material were obtained. Recrystallisation from 98 per cent. alcohol yielded 31.8 grams of pure tetra-acetyl fructose. This compound melted at 129—130°, showed $[a]_D$ in chloroform $- 92.30$, and did not affect potassium permanganate solution even on prolonged action. Attempts to detect mutarotation in chloroform or aqueous solutions of the compound gave negative results even when chloroform or water were substituted for alcohol as the recrystallising media. The tetra-acetyl fructose obtained in this way showed a constant specific rotation in all appropriate solvents.

Examination of Triacetyl Fructose.—After removal of all crystal-

lisable tetra-acetyl fructose from the product of the preparation just described, a large proportion (47 grams) of syrup remained. In order to remove acetic anhydride, this material was boiled for twelve hours under reflux with a large excess of pure dry methyl alcohol. The solution was then neutralised with barium carbonate and, after filtration, concentrated in a vacuum. Extraction with chloroform gave a pale yellow syrup, having $[\alpha]_D$ in chloroform $-20\cdot42$. Analysis of the syrup, dried in a vacuum, gave an acetyl content of $40\cdot41$ per cent., which agrees approximately with the calculated value for a fructose triacetate ($42\cdot15$ per cent.). Attempts to effect further acetylation of the triacetate by repeating the action of acetic anhydride and zinc chloride in the cold failed entirely. The same proportion of the acetylating reagent was used as in the preparation of tetra-acetyl fructose, and the mixture was stirred at $0°$ until a homogeneous system was obtained. Examination of the product showed it to be unaltered in composition or specific rotation. Further evidence that the syrup was a homogeneous compound was afforded by the fact that fractional extraction with solvents failed to separate the material into components showing any differences in rotatory power.

The exact constitution of the compound has not been determined, and it is even impossible to characterise it with certainty as a genuine derivative of fructose. The removal of the acetyl groups required prolonged agitation in the cold with $N/10$-barium hydroxide, the unsubstituted sugar thus obtained being a lævorotatory syrup. This, although readily convertible into phenylglucosazone melting at 203—204°, could not be identified as fructose, and, considering the conditions required for the hydrolysis of the triacetate, was doubtless an equilibrium mixture of glucose, fructose, and mannose.

Methylation of Triacetyl Fructose.

The syrup dissolved readily in methyl iodide and was methylated in the usual manner with the following proportions of the reagents: triacetyl fructose (1 mol.), silver oxide (5 mols.), and methyl iodide (10 mols.). After a second alkylation the product, isolated in the usual manner, was a colourless syrup, which reduced Fehling's solution and was therefore not a derivative of methylfructoside. As the most trustworthy indication of composition is given by the methoxyl and acetyl contents, these values were determined. Found, OMe$=10\cdot6$; OAc$=42\cdot86$.

$C_6H_8O_2(OMe)(OAc)_3$ requires OMe$=9\cdot7$; OAc$=42\cdot15$ per cent.

Solvent.	c.	Specific rotation.
Chloroform	$2\cdot504$	$-21\cdot96$
Ethyl alcohol	$2\cdot230$	$-21\cdot07$

The methylated derivative has thus the composition of a mono-nethyl triacetyl fructose.

XXXI.—*Contributions to the Theory of Solutions. Solubility Studies in Ternary Mixtures of Liquids.*

By JOHN HOLMES.

AN explanation of the property of relative solubility in binary mixtures of liquids has been put forward in previous papers, based on the ascertained difference in magnitude of the molecular volumes of the constituents of the mixture. It was deduced mathematic-ally that so long as the ratio of the radii of the respective mole-cules—assuming them to be capable of representation by a spherical surface—did not exceed the proportion 1·618:1, the liquids would · be miscible in all proportions, and, when the ratio became greater than this value, the mixture would separate into two layers, in each of which the selective distribution of molecules depends on the further increase of this factor until it reaches 2·414:1, when the liquids are now completely immiscible. In practice, the relative solubilities of commonly known liquids were found to be in close agreement with these theoretical deductions, and it seemed reason-able to expect that the extension and application of the same principle to three-component systems would afford an explanation of the somewhat similar solubility phenomena therein observed.

Provided that no chemical interaction occurs between the con-stituents of a ternary mixture of liquids and that no individual liquid influences by its simple physical presence the other con-stituents, any three liquids the molecular spheres of which have equal radii should be miscible in all proportions. When the spheres are of different sizes, as the ratios of the several radii

VOL. CXIII.

M

increase, the dimensions of the interspaces decrease in magnitude until, as in the case of binary mixtures, a point is reached at which close packing is a maximum. In an equimolecular mixture, which lends itself more readily to mathematical demonstration, this occurs when the radii are as $1\cdot682:1\cdot466:1$ (see Figure). It is suggested that when these conditions are fulfilled, the liquids are on the border line between complete and partial miscibility, and that, so long as the ratios between the several radii are not greater than these values, the liquids will be mutually miscible in all proportions. When, however, the respective ratios are greater in magnitude, a complex is formed which will not allow of the same close-packing, but results in the formation of layers of liquid the relative proportions of which depend on the difference in these ratios.

A further consequence of this method of reasoning follows from the known ratio of radii required for the critical point of solution in binary mixtures. So long as the value of the radial ratio of the two smaller molecules is not greater than $1\cdot618$, and the corresponding radius of the larger molecule is greater than $1\cdot682$ and does not exceed $(1\cdot618)^2$, the mixture should separate into two layers only, but if, on the other hand, the respective ratios are greater than these values, and the greater ratio exceeds the less by more than $1\cdot618$ times its value, then the liquids should fall out into three distinct and stable layers.

The object of this communication is to present the results of a preliminary examination into the behaviour of ternary mixtures of liquids from the point of view of these theoretical considerations and of the hypothesis on which this simple law of mixtures is based.

Relative radii, $1 : 1\cdot466 : 1\cdot682$.

EXPERIMENTAL.

In order to determine the critical point of solution in three-component systems, binary mixtures of liquids were first prepared in equimolecular proportions, and the third liquid then added in

quantity sufficient to produce a permanent cloudiness after vigorous shaking. The point of complete miscibility is capable of determination with a high degree of accuracy, since an excess of one drop in a total volume of 25 c.c. invariably causes separation into layers. The several mixtures were made in calibrated stoppered burettes suspended in a water-bath, the temperature of which was kept constant at 15°. Most of the liquids experimented with had been obtained from Kahlbaum, and the usual methods were resorted to for determining their purity.

Mixtures of the lower primary alcohols with water were prepared in equimolecular proportions referred to the gaseous state. The densities of these mixtures at 15·5°/15·5° were found to be CH_4O aq. (1/1) 0·8898, C_2H_6O aq. (1/1) 0·8676, and C_3H_8O aq. (1/1) 0·8601. The radii of the molecular spheres of methyl alcohol, ethyl alcohol, and n-propyl alcohol—represented by the cube roots of the quotients of molecular weight by density—are 1·3, 1·5, and 1·6 respectively when compared with that of water at 15°.

As was to be expected, formic acid, acetic acid, acetone, pyridine, and liquids generally which are miscible in all proportions with water, are similarly miscible with each of the above aqueous-alcoholic mixtures. This applies also to isobutyl alcohol, ethyl acetate, aniline, ethyl ether, and the amyl alcohols, the several radii of which are in slight excess of the theoretical value (1·68).

The following are some of the more important quantitative results obtained.

Mixtures with Aniline.

Proportion by volume of the constituents
of the mixture.

10 c.c. CH_4O aq. (1/1), 16·1 c.c. C_6H_7N, 3·2 c.c. H_2O
10 c.c. C_2H_6O aq. (1/1), 12·3 c.c. C_6H_7N, 5·2 c.c. H_2O
10 c.c. C_3H_8O aq. (1/1), 10·0 c.c. C_6H_7N, 5·7 c.c. H_2O

Critical molecular
mixture.

$C_6H_7N : CH_4O : 2·0 H_2O$
$C_6H_7N : C_2H_6O : 3·1 H_2O$
$C_6H_7N : C_3H_8O : 3·9 H_2O$

The effect of the addition of small quantities of water to these critical mixtures, on the relative proportions of the layers of liquid formed, is very marked. For instance, 20 c.c. of the critical mixture with CH_4O aq. (1/1), to which were added 1·8 c.c. of water, gave after vigorous shaking an upper layer of 6·5 c.c., and a lower layer, coloured with aniline, of 15·3 c.c. Similarly, 20 c.c. of the critical mixture with C_2H_6O aq. (1/1), together with an excess of

1·0 c.c. of water, gave an upper layer of 4·4 c.c., and with 1·9 c.c. of water an upper layer of 7·1 c.c., both lower layers being coloured with aniline. The addition of 2·0 c.c. of water to 20 c.c. of the critical mixture with C_3H_8O aq. (1/1) resulted in an upper layer of 15·5 c.c., which retained the aniline colour, whilst the lower layer was practically colourless; this is the reverse of what happens in the corresponding CH_4O aq. (1/1) mixture. Results very similar to these in character were obtained in other ternary mixtures.

Mixtures with n-Amyl Alcohol.

Proportion by volume of the constituents
of the mixture.

10 c.c. CH_4O aq. (1/1), 19·25 c.c. $C_5H_{12}O$, 3·55 c.c. H_2O.
10 c.c. C_2H_6O aq. (1/1), 14·65 c.c. $C_5H_{12}O$, 3·95 c.c. H_2O.
10 c.c. C_3H_8O aq. (1/1), 12·0 c.c. $C_5H_{12}O$, 3·7 c.c. H_2O.

Critical molecular
mixture.

$C_5H_{12}O : CH_4O : 2·1H_2O.$
$C_5H_{12}O : C_2H_6O : 2·6H_2O.$
$C_5H_{12}O : C_3H_8O : 2·9H_2O.$

The critical molecular mixture of the system ethyl ether with C_2H_6O aq. (1/1) was found to be $C_4H_{10}O : C_2H_6O : 2·6H_2O$, a concentration practically the same as that obtained in the corresponding n-amyl alcohol mixture.

Mixtures of the foregoing liquids in equimolecular proportions afford no evidence therefore of separation into layers at 15°.

The complexities of ethyl ether and n-amyl alcohol, as well as those of the other liquids experimented with above, have been found to be similar to that of water (T., 1913, **103**, 2147); or, if $(H_2O)_n$ be taken as representing the molecule of water in the liquid state, the value of n is the same when applied to the usual formulæ of the other liquids—$(C_5H_{12}O)_n$, $(C_6H_7N)_n$, $(CH_4O)_n$, etc. As will be noticed in the table of liquid complexities given in the communication mentioned above, ethyl ether and n-amyl alcohol have molecular volumes greater in magnitude than those of the other liquids in question, and correspondingly greater radii (1·8 approx.) as compared with that of water. This value is somewhat greater than the theoretical (1·68) required for complete solution. This behaviour is analogous, however, to that observed in binary mixtures of liquids in which the critical point of solution varies within somewhat similar limits, according to the nature of the constituents of the mixture and the magnitude of the volume change which occurs on mixing. That such deviation from theoretical requirements should be obtained was therefore to be expected, since most of these mixtures afford volume changes which vary in degree in different mixtures, and must inevitably result in

some disturbance in the initial relationship of the several molecular spheres.

The admixture of the same aqueous-alcoholic mixtures with liquids having molecular radii greater than 1·8, such as methyl iodide, chloroform, benzene, xylene, carbon disulphide, etc., was found to result in the formation of two layers of liquid. The quantitative data obtained in some of these mixtures are as follows:

Mixtures with Methyl Iodide.

Proportion by volume of the constituents of the mixture.	Critical molecular mixture.
20 c.c. CH_4O aq. (1/1) : 1·55 c.c. CH_3I,	$H_2O : CH_4O : 0·03 (CH_3I)_2$.
20 c.c. C_2H_6O aq. (1/1) : 6·8 c.c. CH_3I,	$H_2O : C_2H_6O : 0·20 (CH_3I)_2$.
20 c.c. C_3H_8O aq. (1/1) : 15·3 c.c. CH_3I,	$H_2O : C_3H_8O : 0·56 (CH_3I)_2$.

Mixtures with Benzene.

20 c.c. CH_4O aq. (1/1) : 1·25 c.c. C_6H_6,	$H_2O : CH_4O : 0·02 (C_6H_6)_2$.
20 c.c. C_2H_6O aq. (1/1) : 7·6 c.c. C_6H_6,	$H_2O : C_2H_6O : 0·16 (C_6H_6)_2$.
20 c.c. C_3H_8O aq. (1/1) : 15·6 c.c. C_6H_6,	$H_2O : C_3H_8O : 0·40 (C_6H_6)_2$.

Mixtures with Carbon Disulphide.

20 c.c. C_2H_6O aq. (1/1) : 2·0 c.c. CS_2,	$H_2O : C_2H_6O : 0·03 (CS_2)_4$.
20 c.c. C_3H_8O aq. (1/1) : 7·9 c.c. CS_2,	$H_2O : C_2H_8O : 0·15 (CS_2)_4$.

According to the method adopted in previous communications for determining liquid complexities, methyl iodide and benzene are doubly complexed as compared with water, and have molecular volumes at 15° of 6·90 and 9·84, with corresponding radial ratios of 1·90 and 2·14 respectively. In the same way, carbon disulphide was found to have four times the complexity of water with a molecular volume of 13·31, and a radial ratio of 2·37. The values given above for critical molecular mixtures are referred therefore to the liquid state. The relative proportions of these liquid molecules in the critical mixtures decrease in the same alcoholic mixture as their molecular volumes increase, whilst the solubility of each liquid increases with the molecular volume of the aliphatic alcohol present.

The critical mixtures of the same liquids with water and *isobutyl* alcohol (mol. vol. 5·1 and radial ratio 1·7) are as follows:

Proportion by volume of the constituents of the mixture.

20 c.c. CS_2 : 7·65 c.c. $C_4H_{10}O$: 0·4 c.c. H_2O.	
20 c.c. C_6H_6 : 10·35 c.c. $C_4H_{10}O$: 0·6 c.c. H_2O.	
20 c.c. CH_3I : 14·8 c.c. $C_4H_{10}O$: 1·1 c.c. H_2O	

Critical molecular mixture.

$(CS_2)_4$: $C_4H_{10}O$: 0·26 H_2O	
$(C_6H_6)_2$: $C_4H_{10}O$: 0·29 H_2O.	
$(CH_3I)_2$: $C_4H_{10}O$: 0·38 H_2O.	

When the liquids in any of these mixtures are present in equi-molecular proportions, two layers only are formed, and their behaviour as regards solubility is in general agreement with theoretical requirements.

Of the critical mixtures containing less than equimolecular pro-portions, those with methyl iodide approximate most closely to the theoretical, just as those containing *n*-amyl alcohol were found to give a corresponding approximation when more than equimolecular proportions are present. The molecular radii of these two liquids, compared with water at 15°, are 1·90 and 1·82 respectively. Hence the radius of the greater molecule in an equimolecular ternary mixture, which is on the border-line between complete and partial miscibility, and of which water and a lower aliphatic alcohol are the other constituents, exceeds that of the smaller molecule by a value intermediate between 1·90 and 1·82, as compared with 1·68 required by theory.

Ternary Mixtures giving Three Liquid Layers.

Little information is to be found in the wide literature relating to the subject of solubility and solutions generally regarding the formation of three stable liquid layers. In commercial analysis, such mixtures are sometimes observed, as, for instance, when castor oil, petroleum, and water or dilute alcohol are shaken together, the castor oil forming an intermediate layer between the aqueous and petroleum layers, in contradistinction to the behaviour of olive oil, which dissolves in the petroleum, so that two layers of liquid only are obtained. Marsh noticed that three layers were formed in the four-component system ethyl ether–water–potassium iodide-mercuric chloride (T., 1910, **97**, 2297), and the equilibrium exist-ing in these mixtures has more recently been investigated by Dunningham (T., 1914, **105**, 368). It is evident that such behaviour of liquids must be classed among the simple facts of solution, and will require adequate explanation by any satisfactory theory of solution. The apparent scarcity of examples of these phenomena is due probably to the fact that no explanation of them is forthcoming from the commonly accepted theories, and that there is little inducement therefore for further investigation in this direction.

According to the principles given above for a simple law of mixtures, the conditions requisite for the formation of three layers in ternary mixtures of liquids must be sought from a consideration of the relative molecular volumes of the liquids present. If the close-packing of molecular spheres in a binary mixture, in which

the ratio of radii is greater than 1·618, results in separation into two layers, it follows that the addition of a third liquid the molecular radius of which is again proportionately greater in magnitude by $(1·618)^2$ should result in the formation of three distinct and stable layers. Stated generally, the required ratios for three-layer formation are $(1·618 + x + y)^2 : (1·618 + x) : 1$, where x and y are positive.

The difficulty immediately arises as to where a liquid is to be found with a radius greater than that of water by at least $(1·618)^2$ or 2·62, since this is the lowest value possible for a three-layer system of which water is one of the constituents. No liquid with so great a molecular volume is given in the table of liquid complexities referred to above. It has been found, however, that members of homologous series, which have hitherto been examined, are similarly aggregated, as, for instance, the aliphatic alcohols and acids and the alkyl iodides, and it is reasonable to assume that members of other series are similar in this respect. From a consideration of the data at present at our disposal, it should be possible to obtain a liquid of suitable molecular volume in the series of paraffin hydrocarbons. There are good grounds for believing that these liquids are doubly aggregated as compared with water (*loc. cit.*), and that their molecular radii increase from *n*-hexane (2·4), *n*-heptane (2·5), etc., as the series is ascended. In these days, the procuring of one of these higher homologues in quantity and sufficiently pure for our purpose is practically impossible. As a compromise, a sample of American petroleum was purified from unsaturated and aromatic compounds and fractionated repeatedly, so as to remove the fractions of lower boiling point. The fraction boiling between 200° and 230° was eventually taken for these experiments. The boiling points of the homologues $C_{11}H_{24}$, $C_{12}H_{26}$, and $C_{13}H_{28}$ are given as 195°, 215°, and 235°, and their calculated radii (assuming double aggregation) are 2·85, 2·92, and 2·99 respectively when compared with water at 15°. It was hoped that the fraction employed would be free from paraffins boiling below 150° (C_9H_{20}, radius 2·7), and the presence of homologues of boiling point higher than 230° is rather advantageous than otherwise to our immediate purpose. In these circumstances, the hydrocarbons present have radii much greater than that required for insolubility in water (2·414), and their relative solubilities, even in methyl alcohol and in ethyl alcohol, are so small that three well-defined and stable layers are readily obtained in the quaternary systems, potassium carbonate–water–methyl alcohol or ethyl alcohol–petroleum.

Among the liquids that have been found to be near the border-

line of complete miscibility with water are aniline, phenol, and nicotine, of which the ascertained radii are approximately 1·7, 1·7, and 1·65 respectively, and each of which is miscible in all proportions within certain limits of temperature.   Mixtures of these liquids with the sample of petroleum were made in the proportions of 90, 50, and 10 per cent. by volume, and exactly one-half of the volume of water was added to each.   The several liquids were measured into narrow glass tubes which could be hermetically sealed, the total volume of the mixture being from 9 to 10 c.c. in each case.   By suspending these tubes in water, the behaviour of the mixtures could be observed up to a temperature of 100°.

Petroleum–Aniline–Water Mixtures.

1. Initial proportions by volume
    of constituents at 15°
    $\left\{\begin{array}{ll}\text{Petroleum} & \text{......} \quad 33·3 \\ \text{Water} & \text{............} \quad 33·3 \\ \text{Aniline} & \text{.........} \quad 33·3\end{array}\right.$

On vigorously shaking this mixture at 5°, three layers of liquid are obtained, the middle aqueous layer being of slightly less volume than the upper and lower layers.   Between 95° and 100°, the aniline displaces the aqueous layer and rises to the middle position, which it retains after further mixing, the three layers being still practically equal in volume.   Gradual cooling causes all three layers to become cloudy, proving that mutual miscibility occurs to some extent.   At low temperatures, the aniline falls again to the bottom, and the original condition of equilibrium is resumed.

2. Initial proportions by volume
    of constituents at 15°
    $\left\{\begin{array}{ll}\text{Petroleum} & \text{......} \quad 6·7 \\ \text{Water} & \text{............} \quad 33·3 \\ \text{Aniline} & \text{............} \quad 60·0\end{array}\right.$

The proportions of the three layers obtained after vigorous mixing at 5° are practically the same as the initial volumes.   Between 95° and 100°, the aniline layer again displaces the hitherto middle aqueous layer, and on mixing at this temperature, dissolves entirely in the petroleum, thus forming two final layers of liquid.   On cooling gradually, the upper petroleum–aniline layer becomes cloudy at 76°, and separates rapidly into two layers, the aniline approaching in volume to its initial proportion and taking up the middle position between the petroleum and aqueous layers.   On further cooling, the aniline eventually falls to the bottom into its original position.

3. Initial proportions by volume
    of constituents at 15°
    $\left\{\begin{array}{ll}\text{Petroleum} & \text{......} \quad 60·0 \\ \text{Water} & \text{............} \quad 33·3 \\ \text{Aniline} & \text{............} \quad 6·7\end{array}\right.$

At 5°, the respective layers have the relative proportions

$\begin{cases} \text{Petroleum layer} & 62 \\ \text{Water layer} & 33 \\ \text{Aniline layer} & 5 \end{cases}$. At 95°, the aniline rises to the middle

position and dissolves in the petroleum, forming two layers of liquid. On cooling, the upper layer becomes cloudy again at 55°, and the subsequent behaviour of the mixture on further cooling is similar to that of the preceding mixtures.

Petroleum–Phenol–Water Mixtures.

1. Initial proportions by volume of constituents at 45° $\begin{cases} \text{Petroleum} & \text{......} & 33\cdot3 \\ \text{Water} & \text{............} & 33\cdot3 \\ \text{Phenol} & \text{............} & 33\cdot3 \end{cases}$

On vigorously shaking this mixture at 5°, three layers of liquid are obtained having the approximate proportions

$\begin{cases} \text{Petroleum layer} & \text{............} & 35 \\ \text{Water layer} & \text{.................} & 22 \\ \text{Phenol layer} & \text{...............} & 43 \end{cases}$

At 90°, the water and phenol are mutually miscible and form with the petroleum a two-layer system. On cooling, the lower aqueous layer becomes cloudy at 71°, and, at immediately lower temperatures, concentrated phenol separates and falls to the bottom, forming three layers again.

2. Initial proportions by volume of constituents at 45° $\begin{cases} \text{Petroleum} & \text{......} & 6\cdot7 \\ \text{Water} & \text{............} & 33\cdot3 \\ \text{Phenol} & \text{............} & 60\cdot0 \end{cases}$

After mixing at 5°, the relative proportions of the three layers are approximately $\begin{cases} \text{Petroleum layer} & 7 \\ \text{Water layer} & 13 \\ \text{Phenol layer} & 80 \end{cases}$ Vigorous shaking at 90°

results in the formation of two layers of liquid. On cooling, the lower aqueous-phenol layer becomes cloudy at 49°, when concentrated phenol commences to fall to the bottom, and three layers are again obtained.

3. Initial proportions by volume of constituents at 45° $\begin{cases} \text{Petroleum} & \text{......} & 60\cdot0 \\ \text{Water} & \text{............} & 33\cdot3 \\ \text{Phenol} & \text{............} & 6\cdot7 \end{cases}$

At 5°, the relative proportions of the three layers obtained after mixing are $\begin{cases} \text{Petroleum layer} & 62 \\ \text{Water layer} & 31 \\ \text{Phenol layer} & 7 \end{cases}$ Above 63°, two layers only are

M*

formed, but below this temperature phenol separates, and three stable layers are again obtained.

Petroleum–Nicotine–Water Mixtures.

1. Initial proportions by volume of constituents at 15° { Petroleum ...... 33·3
Water .... 33·3
Nicotine .... 33·3

After vigorous shaking at 5°, this mixture of liquids separates into two layers having the relative proportions

{ Petroleum layer 36
Aqueous-nicotine layer ... 64

When the mixture is heated to 62°, the lower aqueous layer becomes cloudy and separates rapidly into two layers, a lower layer coloured with nicotine and an intermediate and practically colourless aqueous layer which increases in volume as the temperature rises until, at 90°, the relative proportions are { Petroleum layer 41
Water layer 26
Nicotine layer 33
On mixing at the latter temperature, two layers are again formed, due to the nicotine dissolving in the petroleum. The observed proportions of the layers were now { Petroleum–nicotine layer 67
Aqueous layer 33
Both layers remain clear at temperatures above 63°, but at immediately lower temperatures the nicotine begins to separate from the petroleum and falls to the bottom of the tube, leaving at first a colourless intermediate aqueous layer, which, however, on further cooling, mixes with the nicotine, and the liquids resume their original equilibrium of two layers.

2. Initial proportions by volume of constituents at 15° { Petroleum ...... 6·7
Water .... 33·3
Nicotine .... 60·0

At 5°, this mixture of liquids forms two layers in the relative proportions { Petroleum layer 8
Aqueous-nicotine layer 92. On raising the temperature to 67°, a cloudiness appears in the aqueous layer, and three layers are formed which at 90° have the relative proportions { Petroleum layer 8
Aqueous layer 9 . At 100°, the lower nicotine layer rises to
Nicotine layer 83

he middle position and dissolves in the petroleum, so that on mixng at this temperature two layers again are formed in the proortions

$$\begin{cases} \text{Petroleum--nicotine layer...} & 75 \\ \text{Aqueous layer ....} & 25 \end{cases}$$

)n cooling, the nicotine commences to separate from the petroleum nd fall to the bottom of the tube at 68°, and its general behaviour t lower temperatures is similar to that in the preceding mixture. Very gradual cooling of this mixture results in the formation of our layers at some temperatures. These consist of a small and olourless petroleum layer, then a large layer of petroleum and nicotine, and below these in order a colourless, aqueous layer and t the bottom a concentrated nicotine layer. These layers, however, were clearly metastable, and on mixing gave two stable layers nly.

3. Initial proportions by volume of constituents at 15° $\begin{cases} \text{Petroleum} & \text{......} & 60 \cdot 0 \\ \text{Water} & \text{...........} & 33 \cdot 3 \\ \text{Nicotine} & \text{.........} & 6 \cdot 7 \end{cases}$

At 5°, the proportions of the two layers formed were

$$\begin{cases} \text{Petroleum layer ....} & 60 \\ \text{Aqueous-nicotine layer ...} & 40 \end{cases}$$

Somewhat similar results were obtained with this mixture; the lower aqueous layer becomes cloudy at 76°, and follows the same procedure as in the preceding mixtures.

It will be noticed that at some concentrations the foregoing mixtures of liquids form two layers only, which, within a limited range of temperature, yield three-layer systems, proving how close is the relationship of the molecular volumes of the several liquids to that required by theory for partial miscibility.

These results prove that our theoretical deductions have some foundation in fact, and that with further knowledge of molecular sights in the liquid state it may be possible to predict a three-yer system in ternary mixtures as readily as a two-layer system t the case of binary mixtures of liquids.

The following results were obtained in the three-component stem petroleum--nitrobenzene--water :

1. Initial proportions by volume of constituents at 15° $\begin{cases} \text{Petroleum} & \text{......} & 33 \cdot 3 \\ \text{Water} & \text{...........} & 33 \cdot 3 \\ \text{Nitrobenzene} & \text{...} & 33 \cdot 3 \end{cases}$

On vigorously shaking these liquids at 5°, three layers separat

in the approximate proportions { Petroleum layer 25 / Water layer 32 . Bot / Nitrobenzene layer 43

top and bottom layers are tinged yellow, proving that petroleum and nitrobenzene are mutually miscible to some extent. On heat ing to 90° and again mixing, the nitrobenzene dissolves in th petroleum and two layers are formed, the lower of which is prac tically colourless. On cooling, the nitrobenzene commences t separate from the petroleum at 18°, and at first takes up th middle position, but finally falls to the bottom at about 15°, whe the mixture assumes its original condition of equilibrium.

2. When these liquids are mixed in the relative proportion

{ Petroleum 6·7 / Water 33·3 / Nitrobenzene 60·0 } and { Petroleum 60·0 / Water 33·3 / Nitrobenzene 6·7 } and are vigorousl

shaken, two layers only are formed, and in each case the uppe layer, consisting of petroleum and nitrobenzene, has twice th volume of the lower aqueous layer. No apparent change occur on heating to 100°.

We have no knowledge at present regarding the molecular volum of nitrobenzene in the liquid state, but, according to the law o mixtures now put forward, the results obtained above are con sistent with the view that it is similarly aggregated to aniline an the primary alcohols. Its molecular volume as compared with tha of water at 15° is therefore slightly less than that of n-amy alcohol, namely, 5·65, with a radius of 1·78. These values agre fairly well with its relative solubility, for whereas aniline with molecular radius of 1·71 is miscible with water in all proportion above 167°, the corresponding critical temperature of aqueous nitrobenzene mixtures is 235° (Campetti and Delgrosso, *Mem. R Accad. Sci., Torino*, 1911, [ii], **61**, 187). On the other hand although both liquids are only partly miscible with the petroleum fraction at 15°, nitrobenzene is relatively more soluble than aniline and is miscible in all proportions at a much lower temperature.

Petroleum–Nitrobenzene–Glycerol Mixture.

The complexity of the glycerol molecule has been ascertained t be one-fourth of that of water, and its molecular volume in the liquid state is only slightly greater in magnitude (*loc. cit.*). The difference, however, is sufficiently great to result in glycerol and aniline being miscible in all proportions at ordinary temperatures Nitrobenzene, with a greater molecular volume than aniline, is

only partly miscible with glycerol, so that a three-layer system is
readily obtained with equal volumes of petroleum, nitrobenzene,
and glycerol. At 5°, the approximate proportions of the layers

re   { Petroleum layer   23
     { Nitrobenzene layer 42, the nitrobenzene taking the inter-
     { Glycerol layer   35

mediate position between the petroleum and glycerol.   At tempera-
tures above 17°, two layers only are formed, due to the nitrobenzene
dissolving in the petroleum.

As already stated, these investigations were of a preliminary
nature, their object being to provide data for subsequent deter-
minations of the equilibrium existing in three-layer systems of
liquids.   The work here described was brought to a close in 1915,
and as an early return to it does not seem probable. it was thought
desirable to place on record such results as had been obtained.

In conclusion, I desire to express my indebtedness to Sir J. J.
Dobbie, M.A., LL.D., F.R.S., for facilities afforded me in carrying
on these investigations.

ANNUAL GENERAL MEETING,

THURSDAY, MARCH 21ST, 1918, AT 4.30 P.M.

Professor W. J. POPE, C.B.E., F.R.S., President, in the Chair.

The PRESIDENT announced that Professor Gilbert Thomas Morgan had been nominated by a number of Fellows as a Vice-President, in the place of Lt.-Col. Arthur Smithells.

Dr. A. J. EWINS and Professor A. G. GREEN were elected Scrutators, and the ballot was opened for the election of Officers and Council.

On the motion of Professor H. E. ARMSTRONG, the meeting agreed that the Report of Council, 1917–1918, should be taken as read. The adoption of the Report of Council, together with the Balance Sheet and Statement of Accounts for the year ending December 31st, 1917, was proposed by Sir HERBERT JACKSON, seconded by Dr. A. E. H. TUTTON, and carried.

REPORT OF COUNCIL, 1917—1918.

The Council are gratified to report a substantial increase in the number of Fellows during the past year. On December 31st, 1916, the number of Fellows was 3,198. During 1917, 162 Fellows were elected and 10 reinstated, making a gross total of 3,370. The Society has lost 39 Fellows by death, 14 have resigned, the elections of two have been declared void, and 45 have been removed under the action of Bye-law IV for non-payment of annual subscriptions. The net total number of Fellows, therefore, as at December 31st, 1917, was 3,270, showing an increase of 72. During 1916 there was a decrease in membership of 5.

It is with profound regret they report that the following have either been killed or have died of wounds received in action :—

Arthur Joseph Brearley (1913).
Bertram Haward Buttle (1910).
Norman Phillips Campbell (1913).
Edward William Lanchester Foxell
(1907).

John Maxwell Heron (1908).
Maurice Kemp-Welch (1903).
Herbert King (1897).
Arthur Edwin Tate (1909).

and that the following Fellows have died :—

Andrea Angel (1905).
James Hector Barnes (1905).
William Thirlwall Bayne (1879).
Clayton Beadle (1891).
John Forbes Bell (1907).
Charles Bradshaw (1888).
George Carrington Carrington (1887).
Alexander Macomb Chance (1883).
Taylor Cook (1907).
George Stanley Cooper (1915).
John Kent Crow (1880).
William Ralph Dodd (1886).
Oliver Statham Douse (1911).
John Joseph Eastick (1881).
John Kerr Forrest (1904).
Reginald Le Neve Foster (1872).

Ernest George Hill (1896).
George Thomas Holloway (1886).
Peter MacEwan (1886).
Norman Harry John Miller (1885).
Benjamin Horatio Paul (1868).
Rufus Daniell Pullar (1882).
John Ffraid Richardson (1911).
Henry Charles Stewart-Carlile (1917).
Francis Sutton (1860).
William Henry Symons (1874).
Walter Arthur Voss (1889).
Thomas Utrick Walton (1884).
John Williams (1892).
Charles Henry Wood (1860).
Philip John Worsley (1858).

Resignations have been received from :—

Edward James Caley (1894).
Arthur Carey (1892).
Patrick Carmody (1889).
Tom Peach Colclough (1912).
Walter Bromley Cooley (1888).
Ridsdale Ellis (1912).
Alfred William Gerrard (1875).

Harry Sands Grindley (1906).
Edwin Reginald Hughes (1903).
Norton Henry Humphrys (1883).
Stanley Allen Warrington Okell (1908)
Frederick Alfred Pickworth (1913).
Alfred Oswald Ransome (1910).
William Frothingham Roach (1908).

The hearty congratulations of the Society are offered to Sir William Crookes, Past President, elected a Fellow on December 3rd, 1857, and to Mr. John Frederick Davis, elected December 17th, 1857, who have now been Fellows for over 60 years, and also to the following who have attained their jubilee as Fellows :—

	Elected.
Sir William Phipson Beale, Bart.	Dec. 5, 1867.
Professor Alexander Crum Brown............	Dec. 5, 1867.
Mr. Facundo Joaquin Ramon Carulla	Dec. 5, 1867.
Professor Georg Lunge	Dec. 5, 1867.
Mr. Robert Rattray Tatlock	Dec. 5, 1867.
Professor Herbert McLeod	Feb. 6, 1868.

The volume of Transactions for 1917 contains 1,128 pages, of which 960 pages are occupied by 95 memoirs, the remaining 168

pages being devoted to the Obituary Notices, two lectures on special subjects, the report of the Annual General Meeting, the Presidential Address, and the Table of International Atomic Weights. The volume for the preceding year contained 103 Memoirs occupying 1,212 pages. The Journal for 1917 contains also 2,858 abstracts occupying 1,308 pages, whilst the abstracts for 1916 numbered 3,281 and occupied 1,532 pages. The diminution in the output of chemical memoirs referred to in the last report, continued throughout the year and apparently will be still more marked in the present year. It has still been possible to obtain most of the continental journals for abstraction, and, considering the circumstances, with but little delay.

The abstracts may be classified as follows : —

<div align="center">PART I.</div>

	Pages.	No. of Abstracts
Organic Chemistry	—	886
Physiological Chemistry	—	265
Chemistry of Vegetable Physiology and Agriculture	—	246
	724	1,397

<div align="center">PART II.</div>

General and Physical Chemistry	—	539
Inorganic Chemistry	—	290
Mineralogical Chemistry	—	90
Analytical Chemistry	—	542
	584	1,461
Total in Parts I and II	1,308	2,858

The Council has decided to award the Longstaff Medal for 1918 to Lieut.-Col. Arthur W. Crossley, C.M.G., F.R.S.

During the past year a Joint Committee, comprising representatives of the Chemical Society and the Society of Chemical Industry, has thoroughly explored the possibility of the co-operation of the two Societies in the preparation and publication of abstracts. The Council are glad to report that, as the result of the labours of the Committee, arrangements are now in force which will practically eliminate the overlap hitherto existing in the two sets of abstracts. The editors of the Journals are in touch with one another, and the periodicals coming under review for abstracting purposes are allocated according to an agreed plan.

The economies effected by this scheme of collaboration should be considerable, but still more important, in the view of the Council, is the fact that a beginning has been made in the consolidation of

the interests of the two Societies concerned. The Council feel confident that, especially from this point of view, the new arrangements will be heartily welcomed by the Fellows of the Society. It is earnestly hoped that further developments along the same lines may be found possible, and in particular that, by the joint efforts of the two Societies, the scope of the chemical abstracts published in this country may be extended, and their value correspondingly enhanced.

The two Councils have further given their provisional approval to a scheme whereby the abstracts of each Society would be obtainable, separately and at a reasonable cost, by the members of the other Society. Steps have been taken to ascertain the amount of support likely to be given to this arrangement.

In connection with the Annual Reports, it has been decided to postpone the one dealing with the progress made in Radioactivity during the year 1917 and to publish in 1919 a combined Report for 1917 and 1918. The title of the Branch " Mineralogical Chemistry " has now been changed to " Crystallography and Mineralogy," and in accordance with the announcement made last year, the Report on this Branch appearing in Volume XIV of the Annual Reports covers the years 1916 and 1917.

For the reasons stated in the letter from Sir Edward Thorpe appearing in the Transactions for 1917 (p. 1001), it was decided to reprint the Table of Atomic Weights published in 1916. Dr. Alexander Scott, Sir Edward Thorpe and Sir William A. Tilden have been appointed by the Council to form a Committee to consider and report on a scheme for the future publication of International Atomic Weights.

The usual List of Fellows was not published in 1917 owing to the necessity of economy in the use of paper; but although this is still urgent, it has been considered desirable not to postpone publication for another year.

In view of the smaller number of scientific communications which are available for reading to the Society, the Council have decided that during the present Session the proceedings at three Ordinary Meetings shall be limited to purely formal business, and that on each occasion an Informal Meeting shall immediately follow. By arranging that an Informal Meeting should take place in the evening after the Annual General Meeting, the Council hope to afford added opportunity for personal intercourse among Fellows.

Three Lectures have been arranged for the session 1917–1918. The first of these was given on December 6th by Dr. Frank L. Pyman, who lectured on " The Relation between Chemical Constitution and

Physiological Action," whilst on February 21st Professor the Hon. R. J. Strutt delivered his Lecture entitled " Recent Studies on Active Nitrogen." The Council are pleased to announce that Dr. Horace T. Brown will deliver his Lecture, " The Principles of Diffusion ; their Analogies and Applications," on June 6th next. This Lecture was to have been delivered in March, 1917, but was unfortunately postponed owing to illness of the lecturer.

Fellows will remember that one of the conditions accepted by the Council in receiving the gift of £1,000 to the Research Fund from Mrs. and Miss Müller was that a lecture dealing with the relationship between Chemistry and either Botany or Mineralogy should be delivered once in every three years. The first of these Lectures, to be known as the Hugo Müller Lectures, will be given on April 18th by Sir Henry Miers, who will discourse on " The Old and the New Mineralogy."

The situation created by the orders calling up for military service all men between the ages of 18 and 22, with the exception of engineers, was referred by the Council to the General Committee of Chemical and Allied Societies, who passed the following Resolution :—

> " This Committee desires to associate itself with the Royal Society in their action concerning the calling up of Chemists holding exemption on the recommendation of the Royal Society, and would be glad to take any action which the Royal Society consider would strengthen their hands in the matter."

This resolution was forwarded to the Royal Society. The Council also addressed communications to the War Office and other Government Departments pointing out that chemists were essential to the present and future welfare of the country, and that it would be a mistaken policy to remove them from their present occupations. The General Committee also have before them the question of hastening the release of chemists from the Colours on the cessation of hostilities.

The opinion of the Council on the proposed publication of Chemical Bibliographies in the English language has been requested by a Provisional Committee dealing with this question. The Council, deeming this to be a matter on which the Chemical and Allied Societies should confer, have referred it to the General Committee.

The problem of increasing the use and scope of the Library,

more particularly on the technical side, is engaging the attention of the Council, and the matter has been referred to a Conference of the Representatives of Chemical and Allied Societies for consideration and report. It is hoped that the results of these several deliberations will be issued to Fellows in the near future.

The congratulations of The Chemical Society have been conveyed to Professor S. Hoogewerff, of The Hague, on his attaining his 70th birthday.

Professor Percy F. Frankland and Dr. Alexander Scott have again been appointed to represent the Society on the Board of Scientific Societies.

Sir William A. Tilden has accepted the invitation of the Council to represent the Society on the Court of the University of Bristol.

The number of books borrowed from the Library during 1917 was 2157, as against 1610 the previous year. The additions to the Library comprise 155 books, of which 62 were presented, 282 volumes of periodicals and 54 pamphlets, compared with 115 books, 329 volumes of periodicals and 35 pamphlets in 1916.

The accounts for the year 1917 show a balance of income over expenditure amounting to £1,652 9s. 11d. as against £1,865 19s. 9d. reported last March for the previous year. Whilst the income from all sources was £8,529 18s. 11d., and therefore greater than that for 1916 by £365 19s. 1d., the expenditure exceeded that of 1916 by £579 8s. 11d., and reached the sum of £6,877 9s. 0d. This increase in expenditure is due principally to enhanced cost of producing the various publications, expenses on account of the Journal being £4,420 19s. 2d. as against £4,074 14s. 0d. during 1916, whilst the Annual Reports cost £64 14s. 2d. more than in the previous year. Various items of administrative expenditure have brought the aggregate under this heading from £1,281 5s. 11d. to £1,472 4s. 5d., including an increase from 15 per cent. to 20 per cent. in the war bonus paid to the staff, the provision of library furniture and of a larger supply of stationery ; it has also become necessary to extend the insurance policy from £12,000 to £14,500.

The compensating items of increased income are £82 10s. 0d. on account of subscriptions, £135 11s. 0d. from interest on investments, £100 17s. 6d. from the sale of publications, and £86 9s. 5d. from advertisements in the Journal, the improved dividend on the Society's capital being principally due to the purchase of War Loan with the balance from 1916.

In the Reports for the last two years it has been the practice

to indicate the effect of the War upon the size of the Journal, and this may be brought to date by the following synopsis :—

	Number of Pages.		
	Trans.	Abstr.	Total.
1914...............	2,909	2,068	4,977
1915...............	1,862	1,944	3,806
1916...............	1,368	1,532	2,900
1917...............	1,128	1,308	2,436

It thus appears that the Journal has diminished to just under one-half the pre-war standard, and it is disturbing to find that whilst the cost of printing was £3,230 6s. 6d. in 1914, the corresponding expenditure for 1917 has been £2,543 7s. 9d., an increase of more than 50 per cent. having regard to the relative number of pages concerned. This appreciation is due to the greatly increased cost of paper and to the fact that it has been found necessary to augment the bonus paid to Messrs. Richard Clay and Sons, Limited, which is now 37½ per cent. Valuable assistance has been rendered to the Society, however, by Mr. C. F. Cross, who has recently secured an improvement in the quality of the paper upon which the Journal is printed and has advised the Council in respect of the price which should be paid for it.

One grant only has been made from the Research Fund during 1917, the disbursement being one of £10 as against £94 for 1916, £137 for 1915, and £287 for 1914. Repayments have amounted to £61, and as the dividends have increased by £73, the excess of income over expenditure amounts to £553 2s. 0d. as against £380 17s.9d. for 1916. Early in 1917, £500 War Loan 5 per cent. Stock was purchased with the balance from the previous year, and this capital sum, together with the substantial investment recorded in the previous Report, will help to provide a considerably increased annual amount to be expended upon chemical research when circumstances permit the resumption of normal activities.

A vote of thanks to the Auditors was proposed by the TREASURER and seconded by Dr. G. SENTER, Dr. C. A. KEANE making acknowledgment.

Professor W. A. BONE proposed a vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year. This was seconded by Dr. H. FORSTER MORLEY and acknowledged by Mr. A. CHASTON CHAPMAN.

In presenting the Longstaff Medal to Lt.-Col. ARTHUR W. CROSS-LEY, the PRESIDENT said:

"The introduction of ethyl malonate and ethyl acetoacetate as synthetic agents for the preparation of polymethylene derivatives

BALANCE SHEET.—THE CHEMICAL SOCIETY, 31st DECEMBER, 1917.

Liabilities.

	£ s. d.	£ s. d.
To Subscriptions received in advance	139 3 4	
	3 0 0	142 3 4
		7·29
,, Sundry Creditors		
,, Research Fund:—		
As per last Balance Sheet	13504 1 4	
Add Excess of Income over Expenditure for the year	558 2 0	14357 3 4
,, Chemical Society: Excess of Assets over Liabilities:—		
As per last Balance Sheet	23105 17 6	
Add Excess of Income over Expenditure for the year	1652 9 11	24758 7 5
		£39980 14 8

Assets.

	£ s. d.	£ s. d.
By Investments (value when acquired):—		
£6730 Metropolitan Consolidated 3½ per cent. Stock	7212 8 6	
£1050 London and North Western Railway 3 per cent. Debenture Stock ...	839 12 0	
£1520 1s. 3d. Cardiff Corporation 3 per cent. Stock	1650 1 0	
£1400 India 2½ per cent. Stock	1316 1 0	
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070 2 5	
£4341 Midland Railway 2½ per cent. Preference Stock	3572 2 5	
£1200 Leeds Corporation 3 per cent. Debenture Stock	1148 1 0	
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	1400 13 6	
£1200 North British Railway 3 per cent. Debenture Stock	1088 11 0	
£700 Canada 3½ per cent. Stock, 1930/50 ...	704 8 5	
£2100 5 per cent. War Stock }		
£1100 5 per cent. War Bonds }	3040 0 2	
(Estimated present value of Investments, £16882 2s. 6d.)		24042 0 1
,, Sundry Debtors		861 18 2
,, Subscriptions in Arrear Estimated to realise ...		400 0 0
,, Insurance paid in advance		08 13 4
,, Cash at Bank—Deposit Account	500 0 0	
Less Current Account, overdrawn	271 3 2	228 16 10
,, Cash in hand		22 2 11
,, Research Fund:—		250 19 9
Investments (value when acquired):—		
£1000 North British Railway 4 per cent. No. 1 Preference Stock	1010 0 0	
£4400 Metropolitan Consolidated 3½ per cent. Stock	4587 18 0	
£1034 Great Western Railway 2½ per cent. Debenture Stock	1049 15 11	
£1142 1s. New South Wales 3 per cent. Stock	1000 0 0	
£1132 Metropolitan Water Board 3 per cent. "B" Stock	1002 16 9	
£1365 Midland Railway 2½ per cent. Debenture Stock	1010 6 9	
£806 Victoria 3 per cent. Stock	766 0 2	
£3081 11s. 3d. 5 per cent. War Stock ...	3497 10 1	18364 7 8
(Estimated present value of Research Fund Investments, £19077 5s.)		
,, Cash at Bank		492 16 8
		£39980 14 8

INCOME AND EXPENDITURE ACCOUNT

Income.

	£ s. d.	£ s. d.
To Life Compositions		247 0 0
,, Admission Fees		604 0 0
,, Annual Subscriptions—		
Received in advance, on account of 1917	250 0 0	
,, during 1917 ,, ,, ...	4341 0 0	
,, ,, ,, ,, 1916	366 0 0	
,, ,, ,, ,, 1915 and previous	36 0 0	
	4993 0 0	
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	390 0 0	
	4603 0 0	
Add Arrears at date : 1917, £504 ; 1916 and previous, £554, estimated to realise as per Balance Sheet	400 0 0	
		5003 0 0
,, Lady Subscribers		7 10 0
,, Investments :—		
. Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock ...	176 13 4	
,, £1050 London and North Western Railway 3 per cent. Debenture Stock	23 12 6	
,, £1520 14s. 3d. Cardiff Corporation 3 per cent. Stock ...	34 4 4	
,, £1400 India 2½ per cent. Stock	26 5 0	
,, £2400 Bristol Corporation 2½ per cent. Debenture Stock	45 0 0	
,, £4341 Midland Railway 2½ per cent. Preference Stock	82 15 0	
,, £1200 Leeds Corporation 3 per cent. Debenture Stock...	27 0 0	
,, £1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	33 15 0	
,, £1200 North British Railway 3 per cent. Debenture Stock	27 0 0	
,, £700 Canada 3½ per cent. Stock 1930/50	19 13 9	
,, £3200 5 per cent. War Stock and War Bonds...	122 11 3	
,, Income Tax Recovered	135 8 11	
,, Interest on Deposit Account	36 16 4	
		790 15 5
,, Publication Sales :—		
Journals	1485 19 0	
Proceedings	10 5 0	
Collective Index	54 7 5	
Library Catalogue	1 0 0	
Atomic Weight Tables	5 9	
Annual Reports on Progress of Chemistry	170 18 0	
Memorial Lectures	3 3 3	
	1725 18 5	
Less Publishers' Commission	167 13 2	
		1558 5 3
,, Proceeds of Advertisements in Journal...	£308 6 3	
Less Commission	27 2 6	
		281 3 9
,, Miscellaneous Receipts		4 2 0
,, Subscriptions from other Societies		34 2 6
		£8529 18 11

I have examined the above Accounts with the Books and Vouchers of the Society, and and the Investments.

25, QUEEN VICTORIA STREET, E.C. 4.   W. B. KEEN,
March 4th, 1918.   *Chartered Accountant.*

FOR THE YEAR ENDED 31st DECEMBER, 1917.

Expenditure.

	£	s.	d.	£	s.	d.
By Expenses on account of Journal :—						
Salary of Editor, including Indexing	620	0	0			
Salary of Sub-Editor and Assistant	250	0	0			
Editorial Postages	16	15	1			
Abstractors' Fees	308	12	2			
Printing of Journal	2543	7	9			
Banding	56	6	11			
Printing of Advertisements	104	2	7			
Wrappers and Addressing	4	9	9			
Distribution of Journal	401	2	9			
Authors' Copies	97	0	0			
Insurance of Stock	19	2	2			
				4420	19	2
" Annual Reports on the Progress of Chemistry				435	13	0
" Purchase of back numbers of Journal				5	18	6
" Library Expenses :—						
Salary of Librarian and Assistant...	269	18	0			
Books and Periodicals	193	10	2			
Binding	39	5	9			
				502	13	11
" Indexing for International Catalogue				30	0	0
" Donation to International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological				10	0	0
" Administrative Expenses :—						
Salary of Staff	430	15	0			
War Bonus	201	11	9			
Wages (Commissionaire, Housekeeper, and Charwoman)	187	16	6			
Coal and Lighting	72	15	2			
House Expenses and Repairs	96	4	5			
Furniture	69	12	9			
Tea Expenses	27	3	6			
Insurances	32	0	6			
Accountants' Charges	21	0	0			
Commission on Recovery of Income Tax	6	15	5			
Law Costs	1	1	0			
Miscellaneous Printing	84	5	7			
Stationery	117	5	1			
Postages...	77	12	2			
Miscellaneous Expenses	46	5	7			
				1472	4	5
" Balance, being excess of Income over Expenditure carried to Balance Sheet				1652	9	11

£8529 18 11

certify them to be in accordance therewith. I have also verified the Balance at the Bankers

Approved—CHARLES A. KEANE,
E. W. VOELCKER,
C. F. CROSS.

RESEARCH FUND INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1917.

Income.	£ s. d.	£ s. d.	Expenditure.	£ s. d.
To Dividends on:—			By Grant to H. Wren	10 0 0
£1000 North British Railway 4 per cent. No. 1 Preference Stock	30 0 0		„ Cheque Book	8 0
£4400 Metropolitan Consolidated 3½ per cent. Stock ...	115 10 0		„ Commission on Recovery of Income Tax ...	4 13 0
£1084 Great Western Railway 2½ per cent. Debenture Stock	19 7 8		„ Advertisements	4 14 6
£1142 16s. New South Wales 3 per cent. Stock...	25 14 4		„ Balance, being excess of Income over Expenditure, carried to Balance Sheet	553 2 0
£1122 Metropolitan Water Board 3 per cent. "B" Stock	25 5 0			
£1966 Midland Railway 2½ per cent. Debenture Stock	25 11 10			
£806 Victoria 3 per cent. Stock	18 2 8			
£3681 11s. 3d. 5 per cent. War Loan	169 4 6			
		418 16 0		
(£418 8s. 6d. purchased during year 1917)				
Repayments of Research Grants		61 1 10		
„ Income Tax Recovered		92 19 8		
		£572 17 6		£572 17 6

I have examined the above Account with the Books and Vouchers of the Society, and certify it to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. KEEN, *Chartered Accountant.*

28, QUEEN VICTORIA STREET, E.C.
March 4th, 1918.

Approval—CHARLES A. KEANE,
E. W. VOELCKER,
C. F. CROSS.

heralded an entirely new aspect of organic chemistry. Until some thirty years ago, almost the only closed-chain compounds which had been fundamentally studied were derived from the aromatic hydrocarbons, and the well-recognised stability of the benzene ring had led to the development of a quite specific kind of technique—a technique in which a certain roughness in chemical treatment was permissible. The investigation of the polymethylene derivatives soon showed that these substances called for much more delicate handling.

"Professor Crossley is well known to us as one of the most assiduous workers in this new field. He has contributed to the Society a large number of papers, more especially on dihydrobenzene and hexamethylene derivatives, all of which show evidence of masterly experimentation, and many of which have important bearings on the constitutions of camphor and other components of the essential oils. Much of his earlier work was carried out under conditions which left something to be desired as regards laboratory accommodation and general facilities; British chemistry owes much to men who, like Professor Crossley, have persevered and succeeded, no matter how unfavourable to original work were the conditions under which they were placed in their earlier days.

"Professor Crossley, it affords me great pleasure, in the name of the Council, to hand you the Longstaff medal for original research in chemistry. We hope that the important work upon which you are now engaged will come to an end at no distant date, and that you will then return with fresh vigour to your life-work in the service of our science."

The PRESIDENT then delivered his Address, entitled, "The Future of Pure and Applied Chemistry." Professor H. E. ARMSTRONG moved a vote of thanks to the President for his services in the Chair during the past year and for his Address, coupled with the request that he would allow the Address to be printed in the Transactions. He also expressed the hope that the Council would circulate it among both Houses of Legislature. The motion was seconded by Professor W. H. PERKIN and carried with acclamation, the PRESIDENT making acknowledgment.

The report of the Scrutators was presented, and the PRESIDENT declared that the following had been elected as Officers and Council for the ensuing year:

President.—William Jackson Pope, C.B.E., M.A., D.Sc., F.R.S.
Vice-Presidents who have filled the Office of President.—Henry Edward Armstrong, Ph.D., LL.D., F.R.S.; Alexander Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc.,

F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; Harold Baily Dixon, M.A., Ph.D., F.R.S.; Percy Faraday Frankland, Ph.D., LL.D., F.R.S.; Augustus George Vernon Harcourt, M.A., D.C.L., F.R.S.; William Odling, M.A., M.B., F.R.S.; William Henry Perkin, Sc.D., LL.D., F.R.S.; James Emerson Reynolds, Sc.D., M.D., F.R.S.; Alexander Scott, M.A., D.Sc., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William Augustus Tilden, D.Sc., LL.D., F.R.S.

Vice-Presidents.—Frederick George Donnan, M.A., Ph.D., F.R.S.; George Gerald Henderson, M.A., D.Sc., F.R.S.; Arthur Lapworth, D.Sc., F.R.S.; Arthur Smithells, B.Sc., F.R.S.; William Palmer Wynne, D.Sc., F.R.S.; Sydney Young, D.Sc., F.R.S.

Treasurer.—Martin Onslow Forster, D.Sc., Ph.D., F.R.S.

Secretaries.—Samuel Smiles, D.Sc.; James Charles Philip, M.A., D.Sc., Ph.D.

Foreign Secretary.—Arthur William Crossley, C.M.G., D.Sc., F.R.S.

Ordinary Members of Council.—Julian Levett Baker; Alfred Chaston Chapman; David Leonard Chapman, M.A., F.R.S.; Alexander Findlay, M.A., D.Sc., Ph.D.; Arthur Harden, D.Sc., Ph.D., F.R.S.; Thomas Anderson Henry, D.Sc.; Charles Alexander Hill, B.Sc.; James Colquhoun Irvine, D.Sc., Ph.D.; Sir Herbert Jackson, K.B.E., F.R.S.; Robert Howson Pickard, D.Sc., Ph.D., F.R.S.; Frank Lee Pyman, D.Sc., Ph.D.; Edward William Voelcker.

By WILLIAM JACKSON POPE, C.B.E., M.A., D.Sc., LL.D., F.R.S.

The Future of Pure and Applied Chemistry.

ONE of the most pleasurable events of annual recurrence during my younger days was the Presidential Address to the Chemical Society; it was generally a carefully prepared discourse on some technical subject of which the author was a master, and. always left a lasting impression on the mind of the apprentice to our science. The long list of past Presidential addresses to our Society constitutes a maturely reasoned history of the development of chemistry during the last seventy years.

For three years past pure chemical research has been dormant the whole world over, and it would be difficult for the most accomplished essayist to arrest your attention for an hour by an address on a subject of purely academic interest. Our mental point of view and our outlook upon both present and future are entirely different from those of four years ago; although the present is obscure and painful, the future gives promise of brilliant and rapid developments in natural science in general and in chemistry in particular. In this belief I venture to lay before you some reflections upon the growing recognition of the importance of our science and upon the responsibilities with which, owing to this change in public opinion, our shoulders are laden.

I have often heard the statement made by men who have grown old in the service of science that chemistry, and particularly applied organic chemistry, is a subject in which the British nation can never excel: that minute attention to detail, coupled with the power of organisation and co-operation, entails something antipathetic to the British character; the Germans, we know, have often expressed this view. The events of the last three years have sufficed to dissipate this fallacy for ever. The manner in which Great Britain, caught in the autumn of 1914 with scarcely any resources in the shape of equipment for the manufacture of fine organic chemicals, has rapidly become a larger producer of explosive, pharmaceutical, photographic, and other essential chemicals

than Germany, will remain an enigma to the historian of these present times. The obscurity which surrounds this rapidly exe-cuted operation is not diminished by the existence of difficulties which have naturally acted as inhibiting agents. This country enjoys in a greater measure than any other State a representative Government; in spite of the many advantages of such a form of Government, the fact remains that it necessarily admits of no representation of any phase of public opinion which is not loudly and insistently expressed. Science has always been in this latter position; it has been unvocative. During the first few years of the nineteenth century, Dalton enunciated the atomic theory, Thomas Young stated the undulatory theory of light, and James Watt invented the steam engine, and by these events all the amenities of human life have been revolutionised; indeed, they have exercised vastly more influence on the well-being of our race than did the Napoleonic wars. So accustomed are we, however, to routine habits of thought that most of us would probably answer, in reply to a suddenly posed question, that the battle of Trafalgar was the most pregnant event of the first quarter of the nineteenth century.

A brief moment of reflection would lead us to correct this hasty statement. Sodium was discovered by Davy in 1807, and benzene by Faraday in 1823. From sodium we obtain sodamide, the prime agent in making artificial indigo an economic possibility; the separation of benzene from coal-tar led by logical sequence to the production of Perkin's mauve and of thousands of other synthetic colouring matters, and to the manufacture from coal-tar anthracene of synthetic alizarin, the first heavy blow aimed at the position of the Turkish Empire, involving as it did the ruin of the Turkey-red or madder industry. The first practical process for making alumin-ium depended on the use of Davy's sodium, and with the aid of Davy's safety lamp 250,000,000 tons of coal are mined annually in this country with comparatively slight risk. Faraday's early investigations on the chemical aspects of electrolysis and his studies on magnetic induction led immediately to the invention of the dynamo, and, through Clerk Maxwell, to the introduction of wire-less telegraphy; this one branch of Faraday's investigations, in point of fact, constitutes the ground-work of the whole stupendous vista of results of the general introduction of the electric current into modern life which is so familiar to us all. Cavendish's early pro-duction of nitric acid by the passage of an electric spark through air, reproduced on an enormously larger scale, is now furnishing Central Europe with the nitric acid without which no explosives could be manufactured.

The above-mentioned and multitudes of other fundamental dis-

coveries in physical and chemical science were made almost within a stone's-throw of this room; most of them were made in the Royal Institution, and all of them by an expenditure of money infinitely small as compared with their present-day effects.

Anyone who is in the habit of reading modern historical writers —and they have become quite illuminating since a scientific mode of writing history has been substituted for the older fictional style —knows how political changes, national reforms arising from an effort of the collective conscience, the magnetic influence of some popular demagogue, and the like, are invariably invoked as explanatory of all the vicissitudes of our planet.

The modern historian is here taking a false point of view, and, since he is, in general, quite unacquainted with physical science, his methods are inadequate. The whole history of Europe for the last century has been made within a few hundred yards of Burlington House in our scientific laboratories. One of the most potent incentives to political changes resides in the desire to increase the amenities of life, and research in pure science has had for a hundred years past the greatest influence in facilitating the realisation of that desire. Co-operative effort, one of the most striking aspects of modern life, only became possible when science provided the facilities for municipal power schemes, for telegraphic connexion over the whole world, and for the concentration of production in definite centres. Chemical science is still furnishing the means for further revolutionary changes; during the last few years we have seen great technical developments of purely scientific discoveries—the work of Dewar on the liquefaction of gases, and that of Cross and Bevan on viscose and artificial silk, both of which have led to the profitable utilisation of vast amounts of capital—and it is as yet impossible to indicate the ameliorations of the conditions of human life which will inevitably result from contemporary chemical investigation.

In a time of crisis like the present, British custom tends towards the replacement of unreal conventions by what is really vital; we have been engaged upon this operation for several years. Whilst previously unheard-of changes have succeeded each other kaleidoscopically in the national constitution, in the political parties in power, in the freedom of the subject, and in hosts of other ways, the nation has recognised that science is the only real maker of history. The whole Empire is now one vast chemical and engineering laboratory, and we even live on a scientific ration of so many calorific units. It is obvious that chemistry, with physics, engineering, preventive medicine, and others of the natural sciences, which previously had no imperialistic position, because powerless

to make or break a Government, have become the pivot on which turn all our hopes of retaining an independent national existence; it has been suddenly realised that supremacy in these branches of knowledge is vital to our country.

The time is approaching when this state of affairs will change; neglect of the natural sciences will then no longer put us in danger of sudden extinction, but, as was taking place years ago, will lead to our slow, certain downfall as a nation. The responsibility is placed upon our scientific men of taking such measures as will ensure that the old order is not re-established, that science makes her voice heard in our national councils, and that policies of drift are for ever abandoned.

We have in this country three large and long-established organisations devoted to various phases of chemical science: the Chemical Society, the Society of Chemical Industry, and the Institute of Chemistry. Is it too much to ask that these three representative bodies, with perhaps the newly-founded Association of British Chemical Manufacturers, and ultimately all the other cognate but more specialised interests, should set up a watchful and alert joint Council with directions to consider national questions in which any of the varied interests of chemistry are concerned, and to make such representations to our administrators as would voice the corporate view of the joint body.

I am inclined to think that, had such a body been in existence several years ago, much that has been accomplished in the interval by somewhat devious methods would have been better done. One instance will occur to everyone: that of the much-debated question of the re-establishment of the coal-tar colour industry in Great Britain. The scheme adopted by the Government for resuscitating this phœnix in our country, after its past thirty years of profligate productivity on the Continent, was launched without scientific advice; the Cabinet mouth-piece, indeed, declared that the directorate of the company was not to include men of scientific knowledge, on the ground that a director who knew something about the business of the company would have an advantage over his less well-informed colleagues.

Owing largely to the fact that we possess no strong collective council, representing the combined academic, scientific, and industrial aspects of our science and capable of representing them before a representative Government, it may be argued that we chemists are not altogether blameless for the particularly blundering way in which particular errors have been perpetrated by the responsible officials. Whilst we should be thankful that our blunders have not led to our destruction, we should proceed without further

delay so to organise the resources of chemistry as to make it possible to enforce the adoption of scientific methods and modes of thought by authorities to whom these are yet strange.

The serious character of the British position in connexion with the coal-tar colour industry becomes more evident when one considers that this is a key industry; upon it depend the textile, paper, photographic, and pharmaceutical industries. The total capital employed in the organic dye industry in Great Britain is between four and five million pounds, whilst the capitalisation of the German coal-tar colour firms is of the order of fifty million pounds. The need for greater and more intelligent activity in this direction is obvious; unless national enterprise can be stimulated into providing adequately for the manifold requirements of Great Britain and her Colonies in all those industries which depend on coal-tar colour manufacture, we shall be again in the hands of the foreign producer.

The control of a national dye scheme by business men with no real feeling for the enterprise on which they are engaged renders it fairly certain that the wider aspects of coal-tar colour manufacture will be neglected. The interweaving of the colour interests with those of synthetic pharmaceutical, photographic, and other chemical industries is essential to success. The utilisation and development of the resources of the Empire in natural colouring matters such as indigo is necessary from a national point of view. The careful study of our own and other codes of Patent Law in their bearings upon the fine chemical industry is also important. These weighty questions cannot receive adequate consideration from any purely lay body.

It is mournful but instructive to compare our present position in the coal-tar colour industry with the prospects which that branch of applied chemistry exhibited to Great Britain in early days. The first coal-tar colour was made by Perkin in 1856, and in 1862 Professor A. W. von Hofmann, one of the foremost chemists of the day, a German, domiciled in this country, painted an alluring picture of the future in store for us. Said he: "England will, beyond question, at no distant day, become herself the greatest colour-producing country in the world, nay, by the strangest of revolutions, she may, ere long, send her coal-derived blues to indigo-growing India, her tar-distilled crimsons to cochineal-producing Mexico, etc." When we contrast this dazzling prospect, made by one of the most far-sighted of contemporary German chemists, with the actual situation, we cannot but ask why the event fell so miserably behind the forecast. The reason, in my opinion, lies in the fact that opulent, indolent Great Britain has

for the past century permitted all its educational interests to pass into the hands of a particular caste which despises all knowledge difficult to attain and, to camouflage its own idleness, has always pressed the notion that a first-hand knowledge of the facts of natural science and the conclusions to be drawn therefrom is unimportant, and that the young man or young woman does his or her best in the world if thrown into it entirely destitute of anything but an evanescent acquaintance with certain classics and a decided taste for so-called learned leisure. The greater among the ancients were creators of new knowledge as well as masters of the whole accumulated world's stock of information; their successors, unproductive of positive knowledge and very ignorant of the great changes taking place around them, can but wonder at and comment vaguely on the genius of Archimedes and Aristotle, and necessarily despise the achievements of Newton and Kelvin, their modern prototypes. Illustrations of the stultifying effect of a purely classical education are laid before us every day; one recent example may be quoted here. The gentleman who shares with Mr. A. J. Balfour the honour of representing in Parliament the greatest centre of business and financial activity in the world made the following statement in the House of Commons last Thursday whilst opposing Mr. Fisher's Education Bill: "It was said that education was necessary to make the rising generation good business men. His experience in the City was that the man who took Firsts at Oxford generally came out last, and that the man who could hardly write his name generally came out first. The explanation was that education could not put into a man that instinct of self-preservation and common sense which was the foundation of all success in business. How could education assist a farm labourer to spread manure on a field? The best labourer he had known was wholly illiterate. If the waste of the war was to be replaced it would be necessary for the young to start as early as possible in doing a day's work, instead of wasting time on useless book learning." This representative of the City of London is a baronet of recent creation and a director of one of the largest London banks and of one of the most important English railroads; he received his "education" at one of the oldest and most rigidly classical of our great public schools. Comment is probably unnecessary.

Every scientific man in the world realises that an innate appreciation for fine literature, for great thoughts nobly expressed, and for the appropriate delineation of our greatest aspirations, are among the most sublime instincts of humanity and demand the most careful cultivation. Our literary men say that we cannot

express ourselves effectively, and offer as a satisfying feast the old bones left us by the Greeks and Latins, chewed over for centuries until so devoid of nutriment that they led ultimately to the mental atrophy which characterised the Middle Ages, an atrophy that was only shaken off by the taste for knowledge which arose from the exploits of geographical science in the Elizabethan period.

If the power of expression rests with our literary friends, why are they so idle? It is their obvious duty to devote themselves to popularising the natural knowledge acquired by the scientific observers of the past two centuries; this real learning has so infinitely extended human interest in the world around us and gives such promise of further conquests that an appeal for its consideration would certainly not have been made in vain to Plato or Lucretius. No one asks for the abolition of classical literary learning, but the whole world is now demanding that the young should be provided with an education which includes an insight into our present-day knowledge of the universe.

The rather petty disputes which rage about this matter of classical and scientific education are one-sided; the scientific man generally knows something of both aspects of the subject, whilst his classical compeer rarely has any acquaintance with science. Unfortunately, the great questions involved have more than a petty bearing upon the well-being of our nation. The classical school has held our country in such bondage that, to all practical intent, no person can be admitted to the higher public service unless he swear adhesion to the caste. It is almost regarded as a platitude that acquaintance with natural science disables a man from fulfilling any high public office; practically all the superior positions in the Civil and Diplomatic Services must be filled by men of classical instincts.

I venture to think that the wisdom of this mode of selection has been seriously impugned during the last four years. The huge Government departments which have arisen of late may be divided roughly into two classes—those staffed by men of some scientific training and those staffed by classical university graduates. Anyone who has had occasion to note the numerous recent criticisms on Government departments must have observed that these strictures have almost invariably been passed on administrative branches of the service; delay, the encumbrance of red-tape and inability to draw a decision, seem indigenous in certain Government offices, and none of the numerous attempts at reform has been successful. The administrative services are those in which the classical man is predominant. Other branches, such as the home Army Medical Service, have practically never been charged

with inefficiency; the worst that has been alleged is a suggestion of extravagance.

The department just named is staffed by men who have had, at least, the rudiments of a scientific education; if control in the Royal Army Medical Service had been vested in the classical scholar of ability but no knowledge, it is certain that the last three years would have seen a repetition of the horrors of the Crimean campaign and that the army mortality from disease would have been greater than that caused by the ordinary instruments of war.

Such a control, happily, has been avoided; it has been avoided merely because medicine possesses the collective organisation for which I plead in chemistry, an organisation so strong as to make the imposition of an irresponsible lay control unthinkable.

I have already directed attention to the frequently expressed opinion that, as a nation, we are incapable of excelling in the fine organic chemical industry; let me quote one instance, small in itself, but large in its consequences, in disproof of this view.

The ordinary photographic plate is sensitive only to a region in the blue of the spectrum, but by incorporating certain rather fugitive organic dyes with the sensitive film, the latter may be rendered sensitive to the green, yellow, and red parts of the spectrum; photographic plates so treated are described as panchromatic. The quantities of the sensitising dyes required for the whole world's consumption in normal times is minute, being, indeed, of the order of a few pounds per annum. Until 1915, these substances had never been made outside Central Europe, and little was known by us of their compositions or of the methods of preparing them, as they were all sold under trade names. The manufacture of these materials, small as was the whole business, had been industriously cultivated by the German colour works, and, as these colour sensitisers are essential in aerial photography, their scarcity became of serious import quite early in the war.

The experimental investigation of the whole subject was quickly put in hand in this country, and within a few months ample supplies of the usual sensitisers were produced. Further, the newly established Department of Scientific and Industrial Research financed the development of the study of photographic sensitisers; as a result of this action, new sensitising dyes have been produced which are far superior to the older ones. It is safe to assert that the manufacture of panchromatic plates has now attained a degree of perfection in this country such as will long defy competition.

This is but one case that may be quoted from among a host of others, all of which prove conclusively that, given a little encourage-

ment and assistance, British chemistry is capable, not only of giving much-needed relief in this time of strain, but of meeting every demand which can be made on it when the period of reconstruction commences.

Whilst the absence of the powerful weapon provided by a collective chemical Council, embracing all interests of the science, has made it impossible for us to render the most economical service to our country, it is perhaps satisfactory to reflect that hitherto all that has been sacrificed is economy. Our lack of power to enforce our views has led to financial extravagance on the part of the authorities; the lack of economy in time, which means lives, cannot be attributed to our chemists. The duty will fall to some future President at some later time to record the spontaneity with which the Fellows of this Society volunteered for service in our chemical works, our munition factories, and with the Colours either in our gas service or elsewhere.

One aspect of this question, however, calls loudly for attention. For several years past our teaching staffs have been depleted, and but a small fraction of the normal number of young men have been able to present themselves for training in chemistry. Whilst the present demand for capable young chemists is vastly in excess of the supply, an even more serious situation awaits us in the future. If hostilities were to cease to-morrow, five years would be needed before our colleges and universities could begin to supply the large numbers of young chemists which will be required for the development of the future great fine chemical industry of this country.

Surely this is a matter which should engage the serious attention of the country. If it prove necessary to import young chemists from neutral nations to man our reconstruction schemes a handicap will be established which we may never outrun. The adoption of some scheme by which a sufficient number of juniors can be provided to help in the great developments which the future has in store for the scientific industries of the country is of the utmost importance.

It is impossible to reflect on the desirability of a closer cooperation between the large societies representing chemistry in Great Britain without foreseeing many directions in which such a union would be of value. As in every time of awakening, there exists at present a great feeling of unrest among the younger members of our profession; of late quite a number of propositions for the formation of new scientific societies have been promulgated, and all for the purpose of placing more power in younger hands and for ensuring to the juniors more security of advancement. The final objects of these propositions, so far as I have understood them, are

N 2

entirely praiseworthy, but it is to be feared that the methods sug-
gested for their attainment are not always such as appeal to older
and more experienced people as likely to prove successful. If we
chemists collectively were in possession of some more centralised
organisation, such an one, for example, as is represented by the
Chemists' Club in New York, with facilities for hospitality, meet-
ings, library, laboratory accommodation, and the like, no question
could ever arise of the creation of a new chemical body unconnected
with the main organisation. A new and vigorous issue of the
parent organisation would shoot at appropriate intervals, and
would remain contributing to the strength of the family under the
original patriarchal roof. We greatly need a central home of all
the chemical interests in the country, and premises several times as
large as the Chemical Society rooms, to use as a club, of which
every chemist in the country would be a member. The question of
the necessary expansion of the Library, which is occupying the
earnest attention of your Council, would find an easy solution in
such a pooling of interests.

Notwithstanding that, during the past forty years, much has
been done to facilitate the entrance of talented and promising
young men into the scientific professions, far more progress must
be made in this direction if we are to regain for Great Britain the
paramount position she once held in scientific discovery. The
Natural Science Departments in every University in the country
call for expansion in personnel, laboratory space, and equipment,
and in provision for post-graduate research work; whilst scholar-
ships for students in training are fairly plentiful, the difficulties
which face the advanced student who needs to spend, and who
would benefit immensely by spending, several years on original
research, are often insurmountable. Every professor of chemistry
in the country can recall many instances in which he has had to
send his students into technical life at too early a period, simply
because it has been impossible to secure for a good man the £150
or £200 per annum necessary for living expenses; the provision of
this small sum would, in many cases, convert a half-trained chemist
into a far greater asset to the State.

Whilst a collective effort, exerted by all the interested branches
of our science, to ensure the efficiency of the newly-estab-
lished organisations for furnishing the requisite relief, is urgently
desirable, it should be noted that it will become increasingly diffi-
cult to retain students capable of taking leading positions for a
sufficient time to ensure their proper training. During several
years past I have been visited by gentlemen representing large
chemical industries who have walked round my research labora-

tories to sort out the workers and to make overtures to such as they judged suitable for their own work; the pressure thus exerted upon the universities to force the premature delivery to the works of the best men they have in training will necessarily increase with the coming still greater demand for technical chemists.

The intellectual professions may be roughly classified in two categories: the productive and the parasitic. Those of the productive class, which includes all scientific workers who produce new knowledge, are, in general, poorly remunerated; their practitioners are ordinarily so intensely held by the interest of the work in hand that they have little inclination to divert their energies to the necessary extraction of higher emoluments. The parasitic class, on the other hand, have always been able to command ample remuneration for their labours; the reasons for this difference are various, and need not now be detailed. It may be noted, however, that at the jubilee of this Society in 1891 the veteran, Sir W. R. Grove, who in his young days did so much to develop chemical science, told us that he was led very reluctantly to desert chemistry for the Law because "the necessities of a then large family gradually forced me to follow a more lucrative pursuit." The autobiography of the late Lord Playfair tells a precisely similar tale. Neither of these men is now remembered by anything beyond the great achievements in chemical science of his early days.

The fact emerges that if science is to remain in its service such a proportion of the most powerful intellectual and creative talent of the Empire as will suffice for our progress as a nation, some method must be devised for securing to its followers appropriate emoluments commensurate with those now allocated to the non-productive professions.

This is not only necessary in connexion with those purely utilitarian branches of chemical science to which I have already directed attention, perhaps too insistently, for illustrative purposes. A great danger exists at present, and will grow in the future, that the enormous productiveness of experimental science will overshadow the importance of scientific work of less immediate utility. It would be a great calamity if pure science were neglected in favour of the cultivation only of natural knowledge which gave immediate promise of beneficial material results. One of the most important functions of any expression of collective chemical interests such as I have foreshadowed would be to ensure that pure unproductive scientific research should be retained on an even higher level than that assigned to immediately productive original investigation.

At the present time, physics and chemistry are merging into

one; we foresee that the near future will furnish us with still broader views of the universe and will mark a new development more illuminating even than the great advances which followed Dalton's atomic theory and all its nineteenth century sequences. No material interests must be allowed to check this stupendous expansion of our knowledge.

OBITUARY NOTICES.

ARTHUR JOSEPH BREARLEY.

Born April 1, 1890; Killed in Action June 20th, 1917.

Captain A. J. Brearley, of the Devonshire Regiment, attached Special Brigade Royal Engineers, was reported killed in action on June 20th, 1917. Captain Brearley was a native of Birmingham, being the elder son of Mr. and Mrs. Brearley, of Small Heath, Birmingham. He was educated at King Edward's School, Camp Hill, and the High School, Birmingham, where he obtained several scholarships. He proceeded to Cambridge in 1909, where he was a scholar of Emmanuel College. In 1912 he graduated, having obtained a First Class in Part I. of the Natural Science Tripos and a Second Class in Part II. of the same Tripos. During his university career he rowed and obtained his second May colours.

Prior to the war he was science master at Exeter School. He was granted a commission in April, 1914, being promoted lieutenant in February, 1915, and captain in June of that year. He was transferred to the Royal Engineers in July, 1916, and proceeded to the front in April last year.

His brother, Sec.-Lieut. Norman Blackburn Brearley, Royal Warwickshire Regiment, was killed in action in Mesopotamia in April last year. The only surviving child, Lieut. Selwyn Blackburn Brearley, is serving with the Devonshire Regiment. Captain Brearley was twenty-seven years of age.

BERTRAM HAWARD BUTTLE.

Born March 20th, 1888; Died October 1st, 1917.

By the death from wounds of Bertram Haward Buttle, the Chemical Society has lost one of its younger workers from whom

much might have been expected in the future, whilst those who knew him personally have lost a dear friend for whom they had the greatest respect as well as affection.

Buttle, when first I knew him, was a boy in the former People's Palace Technical Schools. After a short interval at West Ham Polytechnic, he returned to East London College and took the Science Course, graduating with Honours in Chemistry at the B.Sc. examination in 1907. After taking his degree, he went on with post-graduate work, the results appearing in the *Transactions*.*

He took up teaching, and was Science Master at Archbishop Holgate's School, York, when Professor Meldola asked me if I could recommend anyone for a demonstratorship at Finsbury Technical College. Knowing that they both possessed a common characteristic, absolute scientific truthfulness, Buttle seemed the right man, and, as might have been expected, fully justified the choice.

Almost immediately after the outbreak of war, Buttle joined the University and Public Schools Section of the Royal Fusiliers, but was drafted for service in France with the Gas Section of the Royal Engineers in July, 1915. After service with the Mediterranean Expeditionary Force in the winter of 1915—16, he returned to England, obtained his commission in May, 1916, and was in France and Belgium until last autumn, when he was wounded by an aeroplane bomb and died in hospital an hour later.

The letters of sympathy received by his parents give an idea of the impression Buttle gave of his character to those who knew him. The Rev. W. Johnson, formerly headmaster of Archbishop Holgate's School, wrote: "He was such a real man, so thorough and sincere that he gained everybody's affection in my school, both staff and boys. It is rare to find such wisdom with goodness in so young a man, and much as I felt it his advantage to leave me, I mourned his departure from my staff as that of a dear friend.

"His sense of duty was very high and his influence on my boys most excellent."

Major Monier-Williams wrote: "His death is a great grief to me, personally, as I was very much attached to him. He had been with me for several weeks and had always shown the greatest keenness and interest in his work. He was extraordinarily cheerful and willing, and nothing ever seemed to be too much trouble for him. I could always be certain that whatever I gave him to do would be well and thoroughly done."

Captain Bansell referred to the time Buttle served in his com-

* "Solubility of silver chloride in mercuric nitrate solution," 1908, **93**, 1405.

"Constitution of polynitrophenols in alkaline solutions," 1909, **95**, 1775.

pany, " where his courage and never-failing good spirits won him
the love and esteem of all officers and men with whom he came in
contact."

Such was Buttle, honest, industrious, keen on his work, and
always cheerful and ready to do a kind action. Personally, I recall
the many pleasant days spent working together. His friends
mourn his loss deeply.   J. T. HEWITT.

NORMAN PHILLIPS CAMPBELL.

BORN APRIL 25TH, 1886; KILLED IN ACTION MAY 3RD, 1917.

NORMAN PHILLIPS CAMPBELL was the son of Mr. James Campbell,
of Montreal, and was born in Chicago on April 25th, 1886. He
received his early education at the High School, Montreal, at
Cliftonville, Canada, and Dulwich College.

He entered Balliol College, Oxford, in 1904, taking his degree in
1907 and becoming M.A. in 1913. Specialising in physical chem-
istry, he published in collaboration with Hartley papers in this
journal on the solubility of iodine in water (T., 1908, **93**, 741), and
a new apparatus for preparing conductivity water (*ibid.*, 428). In
1908 he decided to go to Ceylon to take up a post under the Church
Missionary Society at Trinity College, Kandy, one of the largest
secondary schools in the colony. On the outward voyage he
carried out an investigation of the salinity of the Indian Ocean
with the aid of Manley's differential densimeter, the results being
subsequently published in the *Proceedings of the Royal Society of
Edinburgh* (**33**, 124).

Campbell worked in Kandy from October, 1908, until the end
of 1914. Although his teaching and duties as a social worker
amongst his pupils (which entered very largely into his life) left
him little time for research work, he carried out an investigation
on the rate of crystal growth, which was published in the *Trans-
actions* for 1915 (T., 1915, **107**, 475).

In December, 1914, he returned to England and enlisted as a
private in the London Scottish, shortly afterwards obtaining a
commission in the Oxfordshire and Buckinghamshire Light
Infantry, and transferring to the Royal Engineers Special Brigade
when it was formed. He was wounded at Loos in 1915, but was
soon able to return to duty. In May, 1916, he was promoted
Temporary Captain; he was killed in action on May 3rd, 1917,
leaving his wife and two young children. His many friends have

cause to lament the death of a man of conspicuous ability and of singular nobility of character, whose death for his country was typical of his life of devotion to others and to his duty.

A. F. J.

EDWARD WILLIAM LANCHESTER FOXELL.

BORN JULY 7TH, 1884; DIED JUNE 11TH, 1917.

EDWARD WILLIAM LANCHESTER FOXELL was the third son of the Rev. W. J. Foxell, Rector of St. Swithin's, E.C. He graduated in science at University College, London, under Sir William Ramsay, and was appointed in 1907 a Master in the Science School and Junior House Master in Christ's Hospital. For many years he was an officer in the O.T.C., becoming O.C. on Colonel Boardman's departure for active service. In Christmas, 1914, he resigned the O.T.C. and was gazetted Captain in the Buffs. During service at the front he fell ill with trench-fever, and died in France of appendicitis on June 11th, 1917.

Those who were so fortunate as to know Mr. Foxell intimately recognised in him a man of versatile attainments. He had a profound appreciation of all that is beautiful, whether in art, literature, or music.

MAURICE KEMP-WELCH.

BORN 1880; KILLED IN ACTION APRIL 11TH, 1917.

MAURICE KEMP-WELCH was born at Bristol in 1880. He was educated at Clifton College and King's College, Cambridge, taking the Natural Science Tripos in 1903. He was an honorary scholar of his College.

On leaving Cambridge, he entered business life, dealing with the commercial chemistry of oils, in which he was greatly interested. He conducted a number of important experiments on wood-oil.

Immediately after the outbreak of war he applied himself to adapting German methods in rubber, and with Mr. Hadfield devised a process of coating canvas with rubber which promised well for the future. Although his concern with these devices was in the first instance commercial, the one characteristic he always showed was science for science' sake. He was on the eve of perfect-

N*

ing some interesting researches in oils when he obeyed his country's call.

He enlisted in November, 1915, in the O.T.C. at Lincoln's Inn. He went to France with the 10th Batt. Yorkshire Regiment in June, 1916, and fought through the battles of the Somme. He was killed on April 11th near Henin-sur-Cojeuil.

Those who knew of his scientific work regret that his ingenuity, which had just begun to produce valuable results, should now be permanently lost.

He married in 1911, and leaves a widow and one daughter.

HERBERT KING.

Born April 7th, 1876; Killed in Action October 6th, 1917.

Herbert King was born in Scarborough in 1876, in which town he received his early education, winning a scholarship to St. Martin's Grammar School, and three years later a County Major Scholarship to the Yorkshire College, the present Leeds University. After a course of three years at the Yorkshire College, he graduated in 1895 as B.Sc. with Honours in Chemistry, and also won the Senior Ackroyd Scholarship, which, however, he resigned in order to take up a teaching post at St. Martin's Grammar School, Scarborough.

He was elected a Fellow of the Chemical Society in 1897. In 1895 he became an Associate of the Institute of Chemistry, and in 1900 was elected to the Fellowship with a special diploma in pharmacology, toxicology, and microscopy. In 1901 he became a M.Sc. (Victoria), and in 1905 a M.Sc. of Leeds University.

He was a member of the Priestley Club and also of the Standing Committee of Convocation of the University of Leeds, the chairmanship of which he resigned on joining his Majesty's Forces in February, 1917.

Between 1897 and 1908 Mr. King held posts as Science Master at Dronfield Grammar School, Sheffield, Ashville College, Harrogate, Wolverhampton Grammar School, and Scarborough Municipal Secondary School. In 1908 he was appointed Head of the Chemical Department of the Cockburn High School and Technical School, Leeds, which post he held to the time of his entering the Army.

From 1909 to the time of his death he was the Public Analyst for Scarborough.

In February, 1917, Mr. King was gazetted to a commission in

the Army Ordnance Department, and after undergoing training in a special course at Woolwich, he was engaged on Government work at Portsmouth, from whence he proceeded to France in August, 1917, and was killed by an enemy bomb on October 6th of the same year. A. J. C.

LEONARD ISON PITT.

BORN 1888; KILLED IN ACTION JULY 30TH, 1915.

A PROMISING life was cut short by the death in action of Leonard Ison Pitt. Pitt received his early education at the Coopers' Company's School, matriculated at an early age, entered East London College in 1904, and took the Final B.Sc. (London) examination in 1908 with First Class Honours in Chemistry, a month or two after his twentieth birthday.

The next year was spent at research work, which was interrupted when Pitt went to Stamford Grammar School as Science Master in 1909; at the time of the outbreak of war he was assistant head at the school. During this period, he took a great interest in agriculture and agricultural chemistry, and passed the first part of the Diploma of Agriculture at Cambridge.

After reading the above record, one might imagine that Pitt's twenty-six years of life up to 1914 had been spent entirely at work. As a matter of fact, he was a very keen sportsman, and especially excelled at football, whilst he took a considerable part in the social life of his college, endearing himself to all who knew him. Pitt was very much alive, and with his witty sayings and pleasing personality kept his immediate neighbours lively as well, whether on the football field or in the research laboratory.

He enlisted at the outbreak of war in the 8th Battalion of the Rifle Brigade, and was very proud of being one of the First Hundred Thousand of Kitchener's Army. By dint of hard work and his power of commanding men, he obtained rapid promotion and became platoon sergeant of " D " Company before many months had elapsed. He embarked for France in May, 1915, and met his death at Hooge while leading his platoon in a counter-attack on July 30th, 1915. The Officer Commanding his platoon writes:

"A better Sergeant or friend no man could wish—he met his death as only an English gentleman can—leading an attack against great odds."

A man of Pitt's great ability and many attainments naturally

N* 2

had a large circle of friends, who, whilst lamenting his death, love
and respect his memory.   J. T. HEWITT.

_____

ARTHUR EDWIN TATE.

DIED APRIL 22ND, 1918.

ARTHUR EDWIN TATE in 1898 entered the Durham College of
Science, now Armstrong College, in the University of Durham,
Newcastle-upon-Tyne, as a student in the Education Department.
He graduated as Bachelor of Science in 1901, with chemistry as
a principal subject. His interest in chemistry was real and living,
and led him to devote his spare time to further work in this subject.
While teaching in the neighbourhood of Newcastle, he worked in
the College laboratories in the evenings and Saturdays, and after
his appointment to the science mastership at Pontefract Grammar
School he continued the experimental investigations thus begun.
In 1909 he submitted the results of this work for the M.Sc.,
and was awarded the degree.   In 1910 he was appointed
senior science master of the City of Norwich School, a position
which he filled with marked success. He joined the Royal En-
gineers in July, 1916, and went to France in the following Sep-
tember, where he was wounded on April 12th, 1917, and died from
the effects of his wounds ten days later. Arthur E. Tate was a
man of sterling qualities, a good and successful teacher. He leaves
a widow, to whom he was married shortly before he joined the
Army.

                                                        P. P. B.

_____

CLAYTON BEADLE.

BORN 1868; DIED AUGUST 16TH, 1917.

CLAYTON BEADLE died at his residence at Sidcup on August 16th,
1917, at the age of forty-nine.

Mr. Beadle had been seriously ill for some time, but recovered
sufficiently to undertake a long foreign tour, partly on business
and partly for recuperation. Although for a time able to resume
his professional duties, he was unfortunately, after a brave
struggle, again laid low, and ultimately succumbed.

Clayton Beadle commenced his chemical career at the works of
his cousin. Mr. Edmund Joynson, the well-known paper maker,

where he studied under Messrs. Cross and Bevan, and formed with them a lifelong friendship. After some time he became a partner in that firm, and during that period he was associated with the various industrial developments of cellulose xanthate or viscose, the name by which it is industrially known.

On the termination of the partnership, Mr. Beadle associated himself with Dr. Stevens, and with him practised as an analytical and consulting chemist. He was not only an expert in the science of paper-making, but was an acknowledged authority on matters connected with the chemistry of rubber, with which branch of industry he was intimately connected.

He also did good work in conserving the water supply of the Kent district. In this connexion, it is interesting to note that his father, Mr. Charles Beadle, gave valuable assistance to the Commission appointed to consider the condition of the lower reaches of the Thames.

Mr. Beadle made numerous contributions to technical literature, and his work was recognised by various societies, including the Royal Society of Arts, La Société d'Encouragement pour l'Industrie National (Paris), and the Franklin Institute (Philadelphia).

ALEXANDER MACOMB CHANCE.

BORN JUNE 28TH, 1844; DIED NOVEMBER 22ND, 1917.

ALEXANDER MACOMB CHANCE, J.P., was the ninth and youngest child of George Chance, of Birmingham, brother of the founders of the well-known firm of Chance Brothers & Co., of Spon Lane and Oldbury. His mother was Cornelia Maria, daughter of Arent Schuyler De Peyster, of New York, in which city George Chance lived for many years as partner with his brother William in trade with the United States.

Alexander Chance was born on June 28th, 1844, after his father's return to England. Having completed his education at Lausanne, he found employment with his relatives at their glass works at Spon Lane. The capacity that he showed soon gained for him, in 1868, the managing direction of their alkali works at Oldbury. In 1879 he was admitted a partner in the firm, and he retained the principal direction of the works, from 1901 as Chairman of the new firm of Chance & Hunt, Limited, until his retirement in June, 1912.

From the start he showed of what metal he was made. Much

wanted doing, and he did it, speedily restoring prosperity to the works and enhancing it as years went on. He was not a man of science; as he himself wrote at the beginning: "I frankly admit that my predisposition is decidedly in favour of commercial negotiations, etc., rather than of the technicalities of manufacture." He was an organiser, a director of industry, able to get the best out of his skilled subordinates by animating them with his own energy and zeal. As has been said of a modern French general, "he radiated vitality." He was ever watchful of all improvements, of new processes, of all means by which production might be increased or losses saved. Of his many successes need only be noticed here his great triumph, the Chance Sulphur Recovery Process. If he did not himself work out the chemistry of this, he directed the experiments and faced the expenditure, and in that sense may be said to have been truly the inventor of it.

Prominent among his characteristics were a singular power of quick and correct decision and a discerning knowledge of men. Those whom he gathered round him in the office, in the laboratory, and in the works formed a staff difficult to match. He treated them as friends rather than as servants, and similarly with the workmen it would be hard to find a master enjoying to a greater degree their goodwill and affection.

In social work for their benefit he was indefatigable. Institutions established at Oldbury before his time, schools, dispensary fund, mission, and relief work, he sedulously fostered, and much else he initiated or promoted, amongst them being religious endeavours, mutual help, sanitary housing, and temperance. The drunkenness that had been rampant at the works he abolished, himself taking the pledge, to the detriment of his health, to set an example. An early achievement was the Convalescent Home at Quinton, a few miles from the works, supported and managed by the men themselves, and regarded by them as their own. Other benefits to them were the Temperance Club and Institute at Langley, and the Provident Accident Fund, which he devised on the passing of the Employers' Liability Act. That Act, he saw, would cover but very few accidents, would involve long delays in its operation, and would be a fertile source of friction between masters and men. Under his scheme, the firm contributed equally with the men to a fund from which the compensation adjudged for each case was paid without question of whose fault, and instantly. One result, not perhaps foreseen, was an extraordinary diminution in the number of accidents. Undoubtedly a sense of personal interest made the men more careful.

These philanthropic activities were by no means limited to Oldbury. Alexander Chance associated himself actively with almost every movement for social advance in Birmingham and its neighbourhood. The cause of temperance found in him an unwearied protagonist. Generous to a fault himself, and giving for the love of it, he had a singular ability of persuading others to give also, and largely. If any fund of importance were to be raised, it became habitual to enlist him early in the cause. It may be questioned whether the money for the Birmingham bishopric could have been raised without his persuasive pressure on rich men. The Birmingham Young Men's Christian Association owes its great modern development and success largely to his efforts. His "St. Andrew's Guild," a work for which he received the thanks in writing of four bishops, transformed one of the worst slum parishes of Birmingham into a model of church organisation and life. His last achievement, pursued to a successful end through years of discouragement, was the acquisition of Warley Park for the use and enjoyment of the public.

His married life was of uniform felicity. His first wife was Florence, daughter of Major Arthur H. H. Mercer, 60th Rifles; his second, Agnes Elizabeth, daughter of William Fleming, of Inverness. Both entered zealously into all his social and philanthropic work. By the former, who died in 1903, he had eight children, of whom four sons and a daughter survive him. His last years he spent in quiet retirement at Torquay, where he died, worn out with work, on November 22nd, 1917.

JOHN JOSEPH EASTICK.

BORN FEBRUARY 6TH, 1855; DIED SEPTEMBER 7TH, 1917.

JOHN JOSEPH EASTICK was born at Great Yarmouth, and in early life had his attention directed to industrial chemistry, his father being manager of the Southtown Gas Works there, and afterwards at Peel, Isle of Man. Before coming to Lancashire and taking up the systematic study of science, he had assimilated the contents of Clegg's "Gas Manufacture," and often took the keenest delight in giving his interested fellow-students an outline of the various operations in the manufacture. The early impressions thus gained lasted through life, and led him to seek the utilisation of chemical results rather than to engage in theoretical research. He gained an exhibition at Owens College and afterwards a Royal Exhibition

at the Royal School of Mines, where he secured the Associateship in Metallurgy.

Instead of following this line, he became first chemist at the sugar refinery of Messrs. Abram Lyle and Sons. From 1890 to 1894 he was manager of the Australasian Sugar Refinery, Melbourne, and acted as honorary adviser to the Victorian Government on beet cultivation and sugar manufacture. Leaving for Queensland, he spent a year on improvements of Messrs. Cran and Tooth's juice mills. During the next ten years, at Millaquin and Yengarie, he was general manager for the Queensland National Bank of their refineries, raw sugar mills, and juice mills and plantations. He was also director and chairman of the Bundaberg distillery for several years and justice of the peace for the territory. In 1906 he inspected tropical and sub-tropical agriculture in the East, but owing to failing health he returned to England.

On the death of Mr. B. E. R. Newlands, his father-in-law, Eastick took over the analytical and consulting practice of Newlands Bros. at No. 2, St. Dunstan's Hill, E.C. He took out a number of patents relating to sugar, and contributed important sections on the theory of filtration and on filtration in sugar factories and refineries to the English edition of Buehler's "Filters and Filter Presses."

Eastick leaves a widow, four daughters, and three sons, the latter of whom are carrying on the traditions of their father in applied chemistry. Tribute will always be paid to his memory by his many pupils, co-workers, and employees, and by all who were acquainted with him for his never-failing kindly advice and aid.

L. J. DE WHALLEY.

ERNEST GEORGE HILL.

BORN FEBRUARY, 1872; DIED JUNE 28TH, 1917.

PROFESSOR ERNEST GEORGE HILL, who died on June 28th, 1917, at the Ramsay Hospital, Naini Tal, from an abscess on the liver, was born in February, 1872, and was educated at Oxford, obtaining the B.A. and B.Sc. degrees of that University.

In 1895 he was appointed to the Indian Educational Service, and took up his duties as Professor of Natural Science at the Muir College, Allahabad, on December 26th of that year. He remained on the staff of the Muir College for the rest of his life. In 1911

he acted as Principal of the College, and was permanently appointed to that post in 1913.

He was for many years a Fellow of the Allahabad University, and was elected Dean of the Faculty of Science.

The Muir College of Allahabad is the most important Government College in the United Provinces, and takes the first place among the Colleges affiliated to the Allahabad University, which controls the college education of the province. The Muir College has always been regarded as a model. The buildings are fine and splendidly situated in beautiful grounds, and teaching work there is not handicapped by the very large classes which make college work so difficult in Calcutta. In these circumstances, and with this environment, Hill took a keen interest in his teaching work and remained throughout his career essentially an educationist.

In order to help his students, he prepared and published tables for qualitative chemical analysis and a handbook of practical chemistry, and his research work in chemistry was undertaken primarily with the object of making the teaching of his subject more real and interesting to his students. About that time Government officials were producing monographs on Indian industries, and Hill's attention was directed to them, with the result that he undertook a number of researches into the constitution of Indian products, and used these to stimulate the interests of his students. As in many other branches of study in India then, the courses of schools and colleges were still too rigidly modelled on European syllabuses, and were apt to be followed by the students as exotic and unpractical studies, necessary for a degree, but of no other value.

Like all those who become seriously interested in University work in India, Hill felt the importance of improving the teaching in schools in order to secure a better foundation for college education, and together with Mrs. Hill he prepared a scientific reader for use in schools.

As Principal of the Muir College and Dean of the Faculty of Science of the University of Allahabad, he was able to exert a very considerable and beneficial influence on education in the province. He was a good disciplinarian, commanding respect from his pupils, whilst at the same time he was on excellent terms with them and with his staff. He was a good cricketer and a keen sportsman; these are very valuable qualifications for anyone responsible for college education in India.

In 1910 and 1911 he rendered valuable services in connexion with the educational section of the Allahabad Exhibition.

Hill's original work in chemistry was directed partly to a study

of Indian products and partly to purely scientific problems of physical chemistry. His interest in the latter is probably to be traced to Oxford, where he returned to work during one of his furloughs. The research work started at this time secured for him the Sc.D. degree of Dublin University. A paper on "The Hydrolysis of Ammonium Salts by Water" (T., 1906, **89**, 1273), and another jointly with Dr. A. P. Sirkar on "The Electrical Conductivity and Density of Solutions of Hydrogen Fluoride" (*Proc. Roy. Soc.*, 1909, [*A*], **83**, 130), indicate the trend of his work in this field.

The first Indian product to attract his attention was the salty and alkaline earth which extends over considerable tracts in Northern India. In 1903 he published a note (P., 1903, **19**, 58) on the analysis of the salts contained in this soil. Afterwards he turned his attention to organic products, and published papers on "The coloured constituents of *Butea frondosa*" (P., 1903, **19**, 133), "A new colouring matter from *Nyctanthes Arbor-tristis*" (T., 1907, **91**, 1501), and "The root bark of *Calotropis gigantea*" (T., 1915, **107**, 1437)—the last two papers being written conjointly with Dr. A. P. Sirkar. The colouring matter from *Nyctanthes Arbor-tristis* was obtained in crystalline condition, assigned the formula $C_{30}H_{26}O_3 \cdot OH$, and named *nyctanthin*. It was subsequently found by A. G. Perkin in *Cedrela toona* (T., 1912, **101**, 1538). From the milky latex which exudes from the broken roots of *Calotropis gigantea*, Hill and Sirkar succeeded in isolating two crystalline substances, melting at 140° and 210° respectively. These were shown to be the *iso*valerates of two alcoholic substances, *mudarol*, $C_{30}H_{47}O \cdot OH$, and *akundarol*, $C_{38}H_{61}O \cdot OH$. These alcohols were shown to give colour reactions very similar to those of cholesterol and phytosterol; on oxidation, they gave mudaric and akundaric acids respectively. In addition to these, the latex was also found to contain an oily substance, a hard, resinous substance, and a trace of alkaloid.

In addition to his work as chemist and educationist, Hill was for some time Meteorological Reporter to the Government. He also took a considerable part in the general life of the City of Allahabad. He was an enthusiastic cricketer and rider in paper-chases, and was very popular with the other Europeans in the station. For some time he was a member of the Municipal Board, where his presence was welcomed by the educated Indians, who appreciated his business capacities.　　　　　E. R. WATSON.

GEORGE THOMAS HOLLOWAY.

BORN OCTOBER 19TH, 1863; DIED OCTOBER 24TH, 1917.

GEORGE THOMAS HOLLOWAY, who died on October 24th, 1917, was born at Battersea on October 19th, 1863, and after being educated privately, entered the Royal College of Science and School of Mines, London, in 1881.   Here he devoted special attention to chemistry, and obtained the Associateship of the Royal College of Science in 1884. He then served for two years as assistant demonstrator, originally under Sir Edward Frankland, and later under Sir T. E. Thorpe. He was elected a Fellow of the Chemical Society on March 4th, 1886. He afterwards proceeded to Newfoundland, and studied the resources of that colony, and also of the east of Canada. Returning to London, he commenced practice in Chancery Lane, in 1888, as analyst, assayer, and consulting metallurgist.   The following year he opened testing works at Limehouse for the examination of ores on a commercial scale. In 1910 his offices and laboratories were removed to 13 Emmett Street, Limehouse. He specialised in the treatment of tin ores and the rarer metals associated therewith. He was consulted by Government departments and many mining companies. Among other work, reference may be made to inquiries, conducted for the Transvaal Chamber of Mines, in connexion with osmiridium occurring in banket ore, and the development of a zinc smelting industry in South Africa. In 1915 he was appointed Chairman of the Royal Ontario Nickel Commission, and to this work the remainder of his life was chiefly devoted.   Despite an enfeebled frame and the dangers from submarines, he twice visited Canada in connexion with this inquiry; he also visited Scandinavia, and interviewed, or corresponded with, all the chief makers and users of nickel in the United Kingdom. The report, which was issued shortly before Mr. Holloway's death, occupies more than 800 pages, and is the most complete and trustworthy document which has appeared in reference to the supplies, extraction, and uses of nickel. As a result of this report, a large nickel refining plant has been established on Lake Erie, at Port Colborne in Ontario. This refinery will deal with Sudbury and other nickel-copper mattes which were formerly refined at New Jersey., U.S.A. Mr. Holloway was for years a frequent attendant at the meetings of the Chemical Society, and was interested in the Institute of Chemistry, for which body he acted as examiner in metallurgy. He was an enthusiastic supporter of the Institute of Metals; but perhaps his fullest sympathy was with the Institution of Mining and Metallurgy, on the council

of which he served for many years, and filled the office of vice-
president. He was a member of the London section of the Society
of Chemical Industry, and a not unfrequent contributor to the
journal of that society. Among other appointments, he had served
as examiner in metallurgy in the University of Birmingham,
assistant examiner to the Board of Education, and juror in the
Franco-British Exhibition of 1900. His clearness of intellect,
kindliness of manner, unassuming character, and perfect honesty
of disposition endeared him to a wide circle of friends, not only
in this country, but throughout the British Empire. He was an
honorary member of the Chemical, Metallurgical, and Mining
Society of South Africa, and acted as corresponding member for
the United Kingdom. With a few words taken from the Journal
of the South African Society this short notice may suitably close:
"It may be fittingly said of him that men of his high character and
conduct do much to raise the status of the profession of which he
was so distinguished a representative."   T. T.

EDMUND ALBERT LETTS.

Born August 27th, 1852; Died February 19th, 1918.

Edmund Albert Letts was born at Sydenham, Kent. His father,
in addition to Clare Lodge in Sydenham, owned South View in
the Isle of Wight, and there Letts appears to have spent the
happiest part of his boyhood, for in later years he often spoke of
the place with affection.

His education began at Bishop Stortford School, and was con-
tinued at King's College, London, after which he studied at the
Universities of Vienna and Berlin.

In 1872 he became chief assistant to Crum Brown in the Chemical
Department of Edinburgh University. Four years later, at the
early age of twenty-four, he was appointed first professor of chem-
istry in University College, Bristol, a post in which he was followed
by Ramsay. In 1879 he was elected to succeed Andrews in the
chair of chemistry in Queen's College, Belfast, and this position
(subsequently changed to a professorship in the Queen's University
of Belfast) he held until 1917. After his retirement, he spent
part of his time in the south of England, and in January, 1918,
he left Belfast on a visit to Ventnor. He was a keen cyclist, and
took his bicycle with him, spending his time riding about the
neighbourhood in which he was staying. On the evening of

February 18th he was out by moonlight, and, while coming down Zig-zag Road about 7.30 p.m., he lost control of his machine and crashed into a wall. He never fully recovered consciousness, and died the following morning about 10 a.m.

His scientific work falls into three main divisions. Up to 1890, his main interest lay among the organic compounds of phosphorus and sulphur, and his investigations in this field gained him the Keith Prize, which was awarded to him in the period 1887—1889 by the Royal Society of Edinburgh. Thereafter he carried out researches on atmospheric carbon dioxide until 1902. His final work was concentrated on the sewage problem, and the results are to be found in Appendix VI. of the 5th Report of the Royal Commission on Sewage Disposal, and also in Appendix III. to the 7th Report of the same body, the work being done in conjunction with Dr. Adeney and Mr. E. H. Richards.

To speak of Letts's personal side is a difficult task for one who only knew him towards the end of his life; but one characteristic stands out above all others—his unfailing kindness to a new and younger colleague. He had complete trust in his staff and showed an unfeigned pleasure in the research output of the laboratory, whether it was his own or was carried out by others, for he had not a spark of that jealousy which at times induces a senior to appropriate the work of a junior colleague. In the distribution of research students among the members of the staff he was more than generous, and his colleagues never had to fear that a student trained by them would be appropriated by Letts as soon as merit was shown. This was not due to indifference, for in his own research room he carried on a steady stream of investigations.

In his personal characteristics, Letts was one of that rare species, "a fine old English gentleman." His reserve, his innate dignity, his impressive presence, and his command of polished oratory all stood him in good stead in the lecture theatre of a university where the students are noted for their high spirits; and the same qualities were valuable to him in other academic relations, for he was one of the leading figures on the staff.

As a chemist, he had a tenacity of purpose so strong that once he had begun an investigation he would never leave it until he was sure that he had carried it as far as he could. "So-and-so used to tell me to drop it," he sometimes said, "but I always find that something comes out if one holds on long enough." He was a neat manipulator and an expert glass-blower.

His outlook on chemistry was a wide one, and his interests tended towards what he called "the philosophy of chemistry." His book. "Some Fundamental Problems of Chemistry, Old and New,"

showed that he was alive to the most recent developments of the subject, and, by its originality in the choice of subjects, it stands apart from the ordinary run of text-books.

He was a Fellow of the Royal Society of Edinburgh and of the Institute of Chemistry. In 1881, the Royal University of Ireland conferred on him, *honoris causa*, the degree of D.Sc., and in 1909, when the Queen's University of Belfast was founded, he was one of the first members of Senate appointed.   A. W. S.

· PETER MacEWAN.

BORN MAY 29TH, 1856; DIED MAY 16TH, 1917.

PETER MacEWAN, of Highgate, London, who was elected a Fellow of the Chemical Society in 1886, was born at Lochee, Forfarshire, on May 29th, 1856. He was educated locally, and was apprenticed to pharmacy with Mr. John Peebles (now Judge Peebles, of Kirkcaldy), and afterwards became an assistant in his uncle's business at Dundee. His instruction in chemistry was obtained under Mr. Frank Young at the Dundee Science Schools, now the Technical College. He passed the qualifying examination of the Pharmaceutical Society in 1878 and became a pharmaceutical chemist in 1880, acting for a short time as a pharmaceutical tutor. An analytical chart for chemistry students which he devised received a wide recognition for utility. In 1882 he was appointed Secretary in Scotland of the Pharmaceutical Society, took charge of the North British branch in Edinburgh, and made all arrangements for the removal to the present premises. A good deal of his time was spent in chemical research work during his tenure of office, one of the first pieces of work being on the iodo-allyl compounds. He was led to take this up by receiving a sample of liniment of iodine which had caused severe blistering when applied to the skin. An investigation showed that the liniment had been compounded with methylated spirit, and he found that allyl alcohol present in the wood spirit used for denaturing purposes had formed an iodo-allyl compound of a particularly irritating nature. Referring to this research, he was fond of recalling how, his eyes streaming with tears, he received visitors to the Pharmaceutical Society's Museum, and it was sometimes assumed that he was suffering from great grief instead of from his devotion to science. The unstable character of sweet spirit of nitre and the changes that take place on keeping attracted his attention. He found that the diuretic

properties of this old galenical were not due entirely to ethyl
nitrite, because old specimens from which ethyl nitrite had dis-
appeared still retained considerable medicinal activity. He
simplified the process of estimating the strength of the spirit, and
when the late A. H. Allen, of Sheffield, devised the nitrometer, it
became possible for the pharmacist to estimate the strength of
sweet spirit of nitre within five minutes. Mr. MacEwan also
directed attention to the large proportion of sodium carbonate,
from 20 to 35 per cent., present in some samples of sodium nitrite,
and showed that there should be no difficulty in obtaining a pro-
duct containing 98 per cent. of sodium nitrite if lead or copper
were employed as deoxidising agents for the nitrate. Several of
his papers dealt with essential oils, particularly camphor oil and
eucalyptus oil, these being at that time recent introductions into
medicine. In after years, Mr. MacEwan often regretted that his
work on camphor oil was not completed, but he had succeeded by
distillation in separating out several of the constituents of this
complex substance. The chemistry of Calabar bean and the pre-
paration of solution of bismuth ammonio-citrate were other
investigations which he undertook, and he substantially enhanced
the interest and value of the scientific meetings of the North
British branch of the Pharmaceutical Society. The allocation of
a portion of the Hanbury collection of Chinese drugs to the
museum caused Mr. MacEwan to take up the study of Chinese,
and he obtained sufficient acquaintance with that difficult language
to enable him to make translations of the labels and classify the
drugs intelligently. In 1885 he was appointed assistant editor of
The Chemist and Druggist, having attracted the attention of the
editor by a clever and laborious codification of the chief pharma-
copœias of the world, which he carried out with the object of form-
ing a basis for an international pharmacopœia. On the retire-
ment of Mr. A. C. Wootton in 1899, he succeeded to the editor-
ship, and from that time specialised in the various legal enact-
ments dealing with the drug trade, for example, the Medicine
Stamp Acts, the poisons laws, the Sale of Food and Drugs Acts,
and the spirit laws, while keeping always in close touch with the
latest developments in chemical and pharmaceutical science. He
contributed a number of papers on ethical subjects to various
pharmaceutical bodies. He visited America in 1893, and made
many friends among American men of science. In 1909 he went
to Germany for the International Congress of Pharmacy, where,
in collaboration with Mr. G. P. Forrester, F.C.S. (who has been
interned in Germany since the outbreak of war), he contributed a
paper on the standardisation of potent medicinal preparations. He

was a member of the Society of Chemical Industry, a corresponding member of the Société de Pharmacie, Paris, Secretary of the Commission on Variation in Activity of Potent Drugs (set up by the International Congress of Applied Chemistry in 1909), and connected with most of the drug trade organisations of this country. Mr. MacEwan was the author of "The Art of Dispensing," which is the standard work in the English language on the dispensing of medicines, and of "Pharmaceutical Formulas," a receipt book for chemists and druggists, of which works many thousand copies have been sold. Of his personal character much could be written, but the outstanding features were his kindness, geniality, "pawky" humour, and indefatigable industry. The strong love of his native country which he had was shown by his yearly visits to the Highlands and his connexion with such bodies as the Scottish Corporation, the Caledonian Society, and the London Forfarshire Association. His end came with great suddenness from an attack of apoplexy, although during the previous winter he had had a severe illness, which acted as a warning. Thus he "laid down the well-worn tools without a sigh" in the plenitude of his powers and with his faculties unimpaired, bequeathing to his friends a lofty ideal and an inspiring example.   S. W. W.

LUDWIG MOND.

BORN MARCH 7TH, 1839; DIED DECEMBER 11TH, 1909.

LUDWIG MOND was born at Cassel on March 7th, 1839. His father, Moritz B. Mond, was a merchant of that city. His mother's maiden name was Henriette Levinsohn.

Mond was educated at the Realschule and the Polytechnic School at Cassel, and then went, in 1855, to study chemistry under Hermann Kolbe at Marburg.

In the following year, 1856, he proceeded to Heidelberg, and so, having followed the great teacher through two institutions, still marked by his influence, he came under the actual control of Robert Wilhelm Bunsen. From him, during a three years' course, Mond undoubtedly acquired that absorbing love of pure chemical science that was so characteristic of him in after life.

His introduction to industrial activity took place at a small Leblanc soda works at Ringenkuhl, near Cassel. Here, the continual waste of sulphur speedily attracted his attention, and he began in 1860 those researches which ultimately led to the invention of his well-known recovery processes.

He left Ringenkuhl to become manager of a factory at Mainz for producing acetic acid by the distillation of wood, and from there went to Cologne to engage in the manufacture of ammonia from waste organic matter, especially leather.

After spending some time in one or two other factories, both in Germany and Holland, he came to England in September, 1862.

Mond's experience at Ringenkuhl led to his patenting a process for the recovery of sulphur from Leblanc alkali waste by atmospheric oxidation, lixiviation, and subsequent separation of sulphur by treatment of the liquors with hydrochloric acid. This process was patented in France in December, 1861, and in England in August, 1862.

Entering the works of John Hutchinson and Co. at Widnes in order to demonstrate the working of his process, and if possible to sell his patent, Mond speedily found that it was not entirely adapted for large-scale operations, where the cost of labour was an important consideration, and he patented an improvement on September 8th, 1863.* This consisted of carrying out the oxidation in the "black-ash" lixiviating vats by blowing air through the waste and repeating the operation after one or two washings with water. Subsequently, Mond introduced the use of waste liquor from chlorine stills in place of fresh hydrochloric acid for the decomposition of the soluble sulphur compounds, with the separation of free sulphur.

In 1864 he undertook the construction and management of a Leblanc soda works at Utrecht, and remained there for three years.

Shortly before his return to Widnes, in 1867, he married his cousin, Frida Löwenthal, daughter of Adolf Löwenthal, who was one of the pioneers of German electro-plating and electro-chemical industry. Lifelong familiarity with scientific problems eminently fitted Mrs. Mond to be the companion of such a man as her husband, and to the end of his life she never failed to take the most intense interest in all his work.

When Mond returned to England, and became a naturalised

---

* "On the manufacture of sulphur from alkali waste in Great Britain," by Ludwig Mond :—Read before the British Association at Norwich, 1868. *Chem. News,* October 2nd, 1868 :—

"On the recovery of sulphur from alkali waste," by Ludwig Mond; Pamphlet published by W. B. Jones & Co., South Castle Street, Liverpool.

"On the probable effect of the general adoption in Great Britain of Mond's process for the Recovery of Sulphur from Alkali waste from a mercantile point of view," being a paper communicated to the River Pollution Commissioners at their request by Ludwig Mond—G. G. Walmsley, 50, Lord Street, Liverpool, 1870.

British subject, he rejoined Messrs. Hutchinson, perfected his sulphur recovery in their works, and introduced it to many others. This and the Schaffner process continued to be worked until they were displaced by the Chance process.[*]

In 1872 Mond made the acquaintance of Ernest Solvay, a Belgian chemist, who was interested in the process of making carbonate of soda invented by Harrison Gray Dyar and John Hemming in 1838.[†] Solvay, in association with his brother Alfred, had built and was running a small factory at Couillet, near to Charleroi. They were not by any means the first who had endeavoured to convert the simple reaction of Dyar and Hemming into a manufacturing process, nor was their experience of difficulties dissimilar from that of their predecessors either on the technical or the financial side; but, by the application of scientific skill, the exercise of boundless patience and tireless application to work, they were beginning to surmount one obstacle after another.

While at Messrs. Hutchinsons' works at Widnes in 1862, Mond had become the friend of Mr. (now the Rt. Hon. Sir) John Tomlinson Brunner, who was in the commercial department of that firm, and when a study of Solvay's works convinced Mond that there were chances of a brilliant future for an ammonia-soda process, he entered into partnership with Brunner and obtained a licence to work Solvay's process in England.[‡]

With some difficulty they obtained sufficient capital to enable them, in 1872, to purchase the Winnington Park Estate, Northwich, from Lord Stanley of Alderley, and to erect small works thereon. Whereas the Leblanc process starts with solid salt, the ammonia-soda process requires salt in solution, and so a Cheshire site was selected for the works, because saturated brine was readily obtainable in the immediate neighbourhood.

With the starting of the works in 1873 there commenced a period of trouble that lasted for six or seven years. Although the reactions $NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl$ and $2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O$ take place most readily as discovered by Dyar and Hemming, the process becomes more complicated when the raw materials are impure, when all operations have to be carried out in closed vessels to avoid loss of ammonia, and when the apparatus itself is apt to be destroyed by the corrosive action of some of the reagents. The problem of convert-

---

[*] G. Lunge, "Sulphuric Acid and Alkali," 2nd edit., 2, 827-851.

[†] Dyar and Hemming, E.P., 7713 of 1838 : Improvements in the manufacture of carbonate of soda.

[‡] E.P., 3131 of 1863, E. Solvay—Apparatus by means of which the formation of carbonate of soda by direct combination is rendered practically available for manufacturing purposes.

ing an interesting chemical experiment into a lucrative commercial process had baffled all the earlier manufacturers, and although Solvay had achieved quite an appreciable measure of success, the gigantic task of evolving an economical continuous process carried on in scientifically designed apparatus was reserved for Mond.

No man was better fitted for the undertaking. Endowed with a quick and fertile brain, he readily grasped the reasons why troubles arose, and his thorough training in pure science enabled him to guard against their recurrence. A tireless worker himself, he had no patience with those whose energies were not sustained. Although his house was within one hundred yards of the works, he frequently spent his nights in the factory, taking such rest as he could secure on a bed arranged in the foreman's office in the midst of the plant. Gifted with powerful determination, he could never contemplate his own failure, and had little sympathy for such as admitted theirs.

A friend was once asking him not to be too hard on a man who had failed to achieve a successful result in a task which had been allotted to him, and urged that the man had done his best, when Mond said: "Heaven help the man who does his best and fails; there is no other hope, and I have no use for him."

By living in the midst of his work, in those early days, Mond set a wonderful example to his assistants and men. His methods of manufacture were absolutely scientific; there was no "rule of thumb" practice. Appearance, taste, and smell did not satisfy him; he took nothing for granted.

One characteristic example is perhaps worth quoting, because it is so typical of his method of teaching in a manner not easily forgotten. Three of his assistants once reported to him that a certain boiler employed for heating brine was constantly getting stopped up with sand. Mond expressed surprise, and accompanied the three to view it. He was shown the sand, and listened for a short time to the various theories propounded of how it came from the brine shaft. He suddenly turned to one and said: "Bring me some hydrochloric acid." When provided with this, he poured it over the "sand," and this promptly dissolved with free evolution of carbon dioxide. Turning to the assistants, he said: "Now where is your sand? You are a nice lot of chemists."

For seven arduous years Mond struggled with the problems which the process presented; but gradually, by successive inventions, he so transformed the methods of manufacture that by the year 1880 he was able to claim that the ammonia-soda process was a commercial success.

Brunner, Mond and Company were not without competitors in

working the Solvay process in England, for, in 1874, Messrs. Richards, Kearne, and Gascoigne had started works at Sandbach in Cheshire, under licence from Solvay. Their venture, however, was not successful, and the works were sold to Brunner, Mond and Company in 1878.

In 1881 the undertaking was converted into a limited company with £600,000 capital, and works at Winnington and Sandbach. Brunner and Mond became managing directors. To-day the nominal capital stands at £10,000,000, and the company owns six factories and has controlling or other interests in several more.

In his endeavour to produce soda more economically by the ammonia process than it could be manufactured by that of Leblanc, Mond was naturally anxious to obtain cheap ammonia. We have seen that, in 1861, he was engaged in the production of ammonia from waste material of animal origin, and he stated that he then observed that the yield by no means corresponded with the nitrogen in the raw material.

In 1879 he determined to make a complete study of the problem of how to manufacture ammonia cheaply.* With the object of testing the value of already known processes for obtaining ammonia from the nitrogen of the air, he engaged Mr. Joseph Hawliczek to carry out the experimental work. All the processes investigated gave unsatisfactory results, with the exception of one, and that was the barium cyanide process invented by Margueritte and Sourdeval. This consists in heating a mixture of barium carbonate with carbon in the presence of nitrogen, and then treating the resulting barium cyanide with steam, thus producing ammonia and regenerating the barium carbonate.

The experiments proved so promising that Mond designed apparatus for carrying out the manufacture on a fairly large scale. The formation of cyanides by this method, however, requires a temperature of from 1200° to 1400°, and Mond ultimately found that his special clay retorts would not last in this great heat, and he was compelled reluctantly to abandon the process. Among the tested processes for obtaining ammonia from the nitrogen of the air was one patented by Rickman and Thompson, who claimed that by passing air and steam through a deep coal fire the nitrogen is to a certain extent converted into ammonia. Mond found that it certainly yielded a considerable quantity of ammonia, but he discovered that, if the same coal were burned in an externally heated tube in a current of steam alone, it gave double the amount. He made large scale experiments in this direction, but came to the

* Presidential Address to the Society of Chemical Industry, 1889, by Ludwig Mond.

conclusion that, although the yield of ammonia was large, the process could never be economical. He saw, however, that if coal could be burned in gas producers by a mixture of air and steam, the plant could be simple, and the gas obtained could be utilised in the same way as ordinary producer gas.

He therefore constructed gas producers and ammonia-absorbing plant at Winnington, and experimented with different classes of fuels for a number of years. These showed that the yield of ammonia varied inversely with the temperature at which the producer was worked, and that the temperature could be controlled by regulating the amount of steam admitted with the blast; the lower the temperature, the higher was the yield of ammonia. Considering the cost of steam, he found that the best practical results were obtained by introducing about two tons of steam for every ton of fuel gasified. He succeeded in converting one-half of the nitrogen existing in the fuel into ammonia, getting about 8 kilos. of ammonia per ton gasified. The gas obtained (now known as "Mond gas") contained about 15 per cent. of carbon dioxide, 10 per cent. of carbon monoxide, 23 per cent. of hydrogen, 3 per cent. of ethylene, and 49 per cent. of nitrogen This was used for heating furnaces and working gas engines, and proved so satisfactory that a large plant was installed at Winnington.

Having now satisfied himself that his process could yield a cheap gas suitable for almost every manufacturing operation, Mond sought to extend its use throughout the world. He formed the Power Gas Corporation to grant licences under his patents, to act as technical advisers to, and erect plants for such manufacturers as desired to employ the gas.

Mond's statement that his gas could be generally employed in manufacture met with strong criticism from iron makers, who said that, on account of its low calorific power, it could never be used for making steel.

With characteristic energy, Mond immediately built a Siemens steel furnace at Winnington and made steel there for some weeks, inviting the steel makers to come and see it.

Recognising that the gas was eminently suitable for small furnace and foundry work, and that it ensured smokeless combustion, Mond was instrumental in founding the South Stafford Mond Gas Company in the heart of the Black Country, at Tipton, near Dudley Port. Here, fuel is gasified in Mond producers, and, after purification, the gas is compressed and delivered into mains that convey it to consumers in about 160 works.

Mond stated in his Presidential Address to the Society of Chemical Industry in 1889 that if one-tenth of the 150 millions

of tons of fuel annually consumed in England were treated by his process, the production of sulphate of ammonia would be large enough to enable us to supply the whole of the Old World, and would render us independent of the New for supplies of nitrate of soda for fertilising purposes. He spoke, of course, in ignorance of the enormous consumption of nitrates which a modern war would involve, but when we, with our later knowledge, recognise the readiness with which an "Ostwald" process can convert ammonia into nitric acid, we can confidently depend upon a moderate development of his process rendering England independent of Chile.

English Mond gas producer works in operation are using bituminous coal, but the Italian installations at Lucca and Orentano are working with lignite.   The process has also been applied to the gasification of peat.

In his anxiety to obtain cheap ammonia for the ammonia-soda process, Mond's attention was attracted to by-product coke ovens, and, as the soda process requires coke for its limestone burning, Brunner, Mond and Company erected the first English installation of Semet-Solvay ovens.

In 1884, Mond made London his regular place of residence in order to live in close association with scientific societies. He first resided in Park Crescent, but later acquired The Poplars, 20, Avenue Road, Regent's Park. This house formed his head-quarters all the rest of his life; there he started a laboratory for his research work, and made his house a centre for scientific and artistic friends. In order to escape the rigours of the English climate, he spent most of his winters in Rome, at his house the Palazzo Zuccari.

One of the first inventions emanating from the new laboratory was a gas battery (*Proc. Roy. Soc.*, 1888, **46**, 296).   Mond obtained the assistance of Dr. Carl Langer, and attempted to discover whether it was possible for a gas so rich in hydrogen as Mond gas to be as directly converted into electricity as pure hydrogen. Starting with the construction of the cell described by Lord Justice Grove in 1839, and working with pure hydrogen, they found that its operation was so tardy that they were led to seek for more suitable electrodes.

After a long series of experiments, they evolved a cell which consisted of a number of elements. The strips of platinum foil as used by Grove, partly immersed in dilute sulphuric acid, gave place to porous diaphragms of inert material, such as plaster of Paris, impregnated with acid, and these were covered on each side with very fine platinum leaf perforated with numerous small holes and covered with a thin film of platinum black. It became

practically a dry battery. A number of these elements are placed side by side with non-conducting frames between to form chambers, so that hydrogen can be passed along one side of the element while the other side is exposed to air.

Mond and Langer found that a battery consisting of seven elements, with a total effective surface of half a square metre, contained 2·5 grams of platinum leaf and 7 grams of platinum black, and gave a current of 2 amperes and 5 volts or 10 watts, equal to nearly 50 per cent. of the total energy obtainable from the hydrogen absorbed. Having so constructed an efficient battery, they next proceeded to employ producer gas in lieu of hydrogen alone. They discovered that unless the gas were deprived of its carbon monoxide and hydrocarbons prior to use, the efficiency of the platinum black rapidly disappeared. In seeking for a cheap method of removing these gases at the temperature of gases leaving the producer, they discovered that if such gases were passed with the steam which they contained over finely divided metallic nickel or cobalt, the carbon monoxide was converted into carbon dioxide and carbon, whilst the hydrocarbons yielded carbon and hydrogen.* They found that when the producer gas was thus purified and enriched in hydrogen it yielded good results with the battery; but, unfortunately, the life of the battery itself proved of short duration.

In connexion with the work on the gas battery, Mond undertook a research in company with Sir William Ramsay and Dr. John Shields on the occlusion of oxygen and hydrogen by platinum and palladium (*Proc. Roy. Soc.*, 1894, **58**; *Phil. Trans.*, 1897, **190**; 1898, **191**).

Pressure of other important work unfortunately prevented Mond from solving the problem of how to construct a battery to endow it with a long life.

By 1886 the ammonia-soda process had developed to such an extent that it had become a serious competitor of the Leblanc process; but as such it possessed one defect, inasmuch as it wasted all the chlorine of the sodium chloride, and so produced no bleaching powder.

This was recognised by Mond as early as 1882, and he patented a process for manufacturing calcium peroxide to be used as a substitute for bleaching powder. He followed this in 1883 by a process for obtaining hydrochloric acid. In the ammonia-soda reaction, the chlorine remains in solution, in combination with ammonia, along with residual sodium chloride. Mond concentrated this liquor by heat, and, after the removal of the first

* L. Mond and C. Langer, "Improvements in obtaining hydrogen," E.P., 12008 of 1888.

.

crystals of common salt, obtained the ammonium chloride in a solid form. This, on treatment with sulphuric acid, yielded hydrochloric acid and ammonium sulphate.

In 1886 (E.P., 66 of 1886) he invented a process for obtaining chlorine by passing the vapour of ammonium chloride over nickel or a similar active oxide to form the corresponding chloride with liberation of ammonia, subsequently treating the chloride with hot dry air to liberate chlorine and regenerate the oxide. By employing superheated steam in place of dry air, he obtained hydrochloric acid instead of chlorine (E.P., 65 of 1886). The process for the manufacture of chlorine was installed at Winnington, and bleaching powder was made by it for several years. The concentration process for obtaining ammonium chloride was superseded by a cold one, wherein the liquors were reduced in temperature by freezing machines until the ammonium salt separated. This was found to yield a product of great purity, an essential property for a salt which had to be volatilised. The dried ammonium chloride was volatilised by heat, and the vapours were passed over nickel oxide. This yielded nickel chloride and allowed free ammonia to pass forward for absorption in water and eventual return to the soda process. Chlorine was obtained by passing a current of hot dry air over the nickel chloride, and was utilised in Deacon chambers for the production of bleaching powder. In order to secure the exposure of a large surface to the action of the gases, Mond made up the nickel oxide into pills by mixing it with china clay and pressing it between rollers with hemispherical cavities. He found that when these pills had been in use for some weeks they became black, swelled up, and ultimately fell into powder. Investigation showed that, in this condition, they contained a considerable quantity of carbon. This was found to owe its origin to the constituents of the so-called "inert gas" which was employed to sweep out the last trace of ammonia from the apparatus before proceeding to evolve chlorine. This gas was obtained from the exits of the ammonia-soda precipitation towers, and consisted of nitrogen mixed with some carbon dioxide and carbon monoxide. A study of the behaviour of these gases in the presence of nickel oxide and their action on metallic nickel led Mond and Langer not only to devise the method previously mentioned of removing carbon monoxide from producer gas, but also to the discovery of nickel carbonyl.*

The plant employed for the volatilisation of ammonium chloride had to be of special construction on account of the violent attack of the vapour on most metals. The valves which were required

* "The history of my process of nickel extraction," by L. Mond, *J. Soc. Chem. Ind.*, 1895, **14**, 945.

for effecting the changes of current were made of nickel. Although laboratory experience had shown this metal to be proof against attack by ammonium chloride vapour, the valves in the manufacturing process soon became leaky, and were found to be coated with carbon. Mond and Langer were thus led to make a careful study of the action of carbon monoxide on nickel with the view of ascertaining whether a definite compound of nickel and carbon was formed. In the course of experiments, finely divided nickel was treated with pure carbon monoxide in a glass tube at varying temperatures for a number of days, and was then cooled in a current of carbon monoxide before it was removed from the tube. In order to keep the poisonous carbon monoxide out of the atmosphere of the laboratory, the gas escaping from the apparatus was connected to a Bunsen burner and lighted. To their surprise they found that, while the tube was cooling, the flame became luminous and the luminosity increased as the temperature fell below 100°. The flame gave a mirror on a cold porcelain plate, and when the glass exit tube of the apparatus was heated, a metallic mirror was obtained inside, whilst the Bunsen flame lost its luminosity. The mirror was found to consist of pure nickel. Eventually they were successful in discovering that, at a temperature below 100°, nickel combines with carbon monoxide to form a tetracarbonyl which is a colourless liquid boiling at 43° and solidifying at 25° to form needle-shaped crystals (Mond, Langer, and Quincke, T., 1890, **57**, 749; Mond and Langer, *ibid.*, 1891, **59**, 1090).

Owing to the disintegration of the nickel pills, Mond substituted magnesia and obtained satisfactory results. The chlorine process was carried on for several years; but the plant proved costly in repairs, and the heat losses were considerable. Although the raw material, ammonium chloride, was ready to hand in solution with other compounds, the separation and drying of the pure salt could not be effected cheaply, and proved a serious handicap to a process which had to compete with those that started with common salt. The process was therefore abandoned in favour of one patented by Carl Hoepfner, by which zinc oxide and calcium chloride under treatment with carbon dioxide yield zinc chloride and calcium carbonate. The zinc chloride on electrolysis gives chlorine and pure zinc. Thus the residual liquors from the ammonia-soda process were made to yield their chlorine, and the zinc was obtained in a state that commanded a high price.

In investigating the properties of nickel carbonyl, Mond was impressed with the ease with which nickel could be converted into a volatile gas by the action of carbon monoxide, and recognised that it might afford a method of separating this metal from others on a manufacturing scale. He was at first averse to undertaking

the creation of an entirely new industry himself so late in life, and proposed to sell his patent; but, as he failed to find a pur. chaser, he erected plant in 1892 in the Wiggin Nickel Works at Smethwick, near Birmingham, and placed it in the charge of Dr. Carl Langer. For such a novel process, all the plant had to be designed and constantly altered through the first four years of arduous work. When the practicability of the process had been fully demonstrated, Mond formed the Mond Nickel Company, and handed over to it the future developments of the manufacture. He became its first chairman, and retained the office until his death. In addition to the labour involved by the construction of large works at Clydach, near Swansea, the company had to acquire and develop mines and ore-handling plant in Ontario, Canada. Although in all this work he was ably assisted by his two sons, together with Dr. Langer and Dr. B. Mohr, the bulk of the work fell upon Mond, for, with his characteristic thoroughness, he insisted upon personally examining every detail.

He had the satisfaction of seeing his process become of immense commercial importance, and the company rewarded with phenomenal success. The Clydach Works, managed by Dr. Langer, have been repeatedly enlarged, and now produce annually upwards of 3000 tons of 99·9 per cent. nickel.

The details of the process were well described by Roberts-Austen before the Institute of Civil Engineers in 1898 (*Proc. Inst. Civil Eng.*, 1898, 135). The discovery of such an astonishing compound as nickel carbonyl led Mond to investigate the action of carbon monoxide on other metals. He soon succeeded in preparing iron carbonyl, but found that, at the ordinary pressure, no results were obtained with any of the large number of metals which he employed. At high temperature and under extreme pressure, however, he succeeded later in obtaining carbonyl of cobalt at 100 atmospheres and 200°, of molybdenum at 250 atmospheres and 200°, and of ruthenium at 450 atmospheres and 300° (*Seventh Inter. Congress App. Chem.*, 1909).

The account of this work, carried out with the assistance of Dr. Hirtz and Mr. Cowap, formed the substance of the last publication under Mond's name (T., 1910, **97**, 798).

The four strenuous years devoted to the placing of the nickel process upon a firm industrial basis undoubtedly overtaxed Mond's strength. He had suffered from a weak heart for several years. The unfortunate death of three workmen, due to inhaling some of the poisonous nickel carbonyl, deeply affected him, and the sudden death in Egypt of his daughter-in-law, Mrs. Robert Mond, completely broke him down.

He presided over the Inorganic Section of the Seventh Inter-

national Congress of Applied Chemistry held in London in the summer of 1909, and entertained the members at a garden party at The Poplars, Avenue Road. In the late autumn he suffered much from sleeplessness, and his health visibly declined. He had intended to winter in Rome, but was never sufficiently well to bear the journey. He died at his house on December 11th in his seventy-first year, and was laid to rest on the 14th in the mausoleum at Finchley, which he had built to receive the bodies of himself and his family. The funeral was most impressive. Standing on the top of the wide stone steps which lead to the upper part of the mausoleum, the Jewish Rabbi conducted the service in Hebrew. Ranged below him stood men eminent in science, art, and industry; Mond's two sons, his old partner and friend Sir John Brunner, Ernest Solvay, directors, managers, foremen, and old workmen from the factories with which he was connected, and chemical manufacturers. These, from far and near, along with a group of chemists containing those who had been associated with him in his researches, seemed to represent every phase of his life. Whatever was the sense of personal loss, each felt that science and industry had lost a great man. He was recognised by all as an ideal industrial pioneer. With all his love of pure science, he was never led to make interesting researches which had no definite object. He never undertook work which was unlikely to prove of industrial utility. His financial success was great, but this was not regarded by him as the reward which he desired for his work. He never worked for the purpose of making money, but for the sole object of cheapening manufactured products. In his fortuitous partnership he owed his financial success just as much to the commercial genius of Sir John Brunner as the latter, in turn, was indebted to the scientific ability of Mond.

No words can more fitly describe Mond's attitude of mind in connexion with his work than those used by himself in concluding his presidential address to the Society of Chemical Industry in 1889. He said:

"The statement is frequently made that 'Necessity is the mother of Invention.' If this has been the case in the past, I think it is no longer so in our days, since science has made us acquainted with the correlation of forces, teaching us what amount of energy we utilise, and how much we waste in our various methods for attaining certain objects, and indicating to us where and in what direction, and how far, improvement is possible; and since the increase in our knowledge of the properties of matter enables us to form an opinion beforehand as to the substances we have available for obtaining a desired result. We can now foresee, in most cases, in what direction progress in technology will move, and, in con-

sequence, the inventor is now frequently in advance of the want, of his time. He may even create new wants, to my mind a distinct step in the development of human culture. It can then no longer be stated that 'Necessity is the mother of Invention'; but I think it may truly be said that the *steady methodical investigation of natural phenomena is the father of industrial progress*."

He had no great faith in the value of teaching technological or industrial chemistry in special laboratories or institutions, for he held that a man could only become a successful industrial chemist when he had received a complete training in pure science.

In his speech to the students assembled at the opening of the Schorlemmer Laboratory for Organic Chemistry, Manchester, in May, 1895, he advised them to devote their attention to the study of pure science alone without giving any thought to immediate practical results.

In order to foster scientific research, Mond purchased a house, formerly the town residence of Lord Albemarle, adjacent to the Royal Institution, and after converting it into a laboratory, fully equipped with apparatus at a cost of £45,000, presented it to the nation along with a sum of £62,000 as endowment, requesting that the building should be called the Davy-Faraday Laboratory. His idea was to provide a place where an investigator could secure the means of pursuing his researches under the best possible conditions without the expenditure of large sums of money.

All through his life Mond never failed to point out to his assistants that, in order to avoid waste of time and for the purpose of securing a favourable start, they should read all that had been published on the subject before they started any new investigation. In his later years, he recognised that in the face of the multiplication of scientific publications it became year by year more difficult to ascertain what had been written. In order therefore to facilitate the consultation of the world's publications, he presented the Royal Society with a sum of £14,000 to defray the cost of the regular compilation of a catalogue of international scientific literature.

Great as was the fortune which Mond amassed, no less princely was his liberality. What he gave privately to those on whom fortune had not smiled is known to very few. It is, however, certain that of those who solicited help from him, none but such as were proved to be unworthy failed to receive it.

Mond was the recipient of the following honours:

He was instrumental in founding the Society of Chemical Industry, and was elected its first president in 1881, and was again president in 1889.

He was elected a Fellow of the Royal Society in 1891.

Doctor of Science (*honoris causa*) of the University of Padua in 1892.

Doctor of Science (*honoris causa*) of the University of Heidelberg in 1896.

Foreign member of the Reale Accademia dei Lincei of Rome in 1899.

Doctor of Science (*honoris causa*) of the University of Manchester in 1904.

LL.D. (*honoris causa*) of the University of Oxford in 1907.

Honorary member of the German Chemical Society in 1908.

Grand Cordon of the Crown of Italy in 1908.

Honorary foreign member of the Royal Society of Naples in 1908.

Foreign member of the Prussian Academy of Science in 1909.

Ludwig Mond was a man with a most impressive presence. He had a large head with a highly developed forehead. Although he was bald on the crown, his hair grew profusely round his neck and always evinced a tendency to curl. His eyebrows were thick and protruded somewhat over his dark, piercing eyes. His beard was full and his features generally were of an Oriental type. His face was capable of expressing extreme gentleness and intense severity. He had a keen appreciation of humour, and in his younger days was almost boyish in his mirth. He possessed a most sociable disposition, formed firm and lasting friendships, and ever preserved a tender regard for those with whom he had associated.

He possessed a sensitive and sympathetic nature, and was ever ready to assist those who were in trouble. He was a keen debater, but very quick in resenting obvious contradiction. The powerful will and firm self-confidence that enabled him to achieve so much made him disinclined readily to weigh other people's opinions against his own. A rapid thinker himself, endowed with a remarkable faculty for mental arithmetic, he was apt to become impatient with those who failed to follow. For him, all information had to be definite and precise; generalities annoyed him. He could not think of a problem unless he had volumes, weights, and temperatures to commence with.

His voice was deep and guttural, and he never so completely lost his German accent as to master the English "w's" and "th's." He possessed the power of obtaining sleep at will, and although an indefatigable brain worker, he could reinvigorate himself by taking half an hour of sleep, terminating almost at the moment he had arranged.

He was a great cigar smoker, and obtained stimulus from the practice. His consumption of a cigar kept pace with the working of his brain. When engaged in the discussion of abstruse problems,

he invariably walked up and down his room smoking, and as he became more and more absorbed in thought, his cigar burned faster and faster.

He was much beloved by his workpeople, who regarded him as an exacting master, but a perfectly just one. He could be, and often was, very angry with any man who was lazy or stupid, but he never kept any bitter feeling towards the delinquent. Much of his anger, too, was assumed for the purpose of making an impression.

During his absence in Rome in 1903, a report reached England that he had died, and obituary notices appeared in some of the newspapers. The news was quickly shown to be false, and on his next visit to Winnington the workpeople met him in torchlight procession, presented an illuminated address of welcome, and made Winnington Park gay with fireworks.

In 1898, to celebrate the twenty-fifth anniversary of the commencement of the works, Sir John Brunner and Dr. Mond presented a handsome building to the company to serve as a pavilion and recreation club for the workpeople. . It was built in Winnington Park on the recreation ground. They further entertained their men with their wives and children, to the number of 12,000 individuals, at a *fête* in the park.

His winter residence in Rome developed that great love of the arts which had always been characteristic of him. He was intensely fond of music, and never so happy as when he could offer his hospitality to those who were celebrated in the art.

He was a great admirer of the early Italian painters, and he collected at his London house one of the finest galleries of their works in England. At his death he bequeathed these to the nation.

In an eloquent commemoration of their foreign member, Ludwig Mond, read to the Dei Lincei Royal Academy on April 3rd, 1910, by Raffaele Nasini, the author said :

"He loved Italy with a great love; he loved it on account of its brilliant skies, on account of its beautiful landscapes, the customs of the people, and its ancient art; he loved it in its men of science, in its men of literature, in its men of art. He assisted many provident and charitable institutions in this country; he relieved many disasters great and small, together with his good companion. Italians found in his hospitable house at The Poplars a piece of their own country, where everything spoke of Italy. How many glad remembrances of our country and our countrymen were evoked by Dr. Mond and his amiable family; how much admiration for Italy burst forth from their hearts whilst the Virgin of Tiziano and the beautiful Flora of Palmo il Vecchio were smiling on us.

"Italian science was a great favourite with Mond, and conspicuous grants were received from him by the Chemical Institute of Rome and my Institutes of Padua and Pisa.

"For our grand Cannizzaro he had an intense admiration and profound veneration. He said that his friendship with him was one of the greatest satisfactions of his life. In honour of Cannizzaro he founded in our Academy that conspicuous prize called after him, which will be delivered the first time in 1911, and let it be hoped that it will bear fruit equal to the love entertained for science by him who founded it. Last year (1909) the Italians who met in London for the International Congress of Applied Chemistry wished to show their gratitude to Mond, and on May 30th, in connexion with a splendid garden party given by Mond to the members of the Congress, there was offered to him, on behalf of nearly 500 chemists of our country, a bronze shield, the eminent work of our sculptor, Carlo Fontana, on which Mond's work was symbolised. On presenting it, speeches were made by Professor Ciamician, myself, and Professor Paternò, the latter expressing himself in very appropriate language as follows:

"The prize you have founded and which you wish to adorn with the illustrious name of Stanislas Cannizzaro will be for Italian chemists, now and for ever, a perennial monument of their gratitude towards you. The honour shown to our grand master is an indissoluble link between your name and Italian Science.

Mond in his reply remarked that what he had had in view was to point out to the present and future generations of chemists what splendid results may be obtained from a life of true devotion to science such as had been, and was, that of Cannizzaro."

In addition to the portrait of Mond on the shield mentioned above, there are a marble bust (1896) by Joseph von Kopf, a bronze bust by Henri Glicenstein, a bronze statue (1906) by Ferdinand Seeboeck, a portrait medallion by E. Lanteri (1911), an oil painting by Solomon J. Solomon, R.A., and in Winnington Park stands a lifelike bronze statue by E. Lanteri, unveiled by Sir John Brunner in 1913 amid a remarkable concourse of Mond's old friends. Here, from his granite pedestal, wearing his well-known dust coat and patriarchal soft felt hat, holding a bundle of plans in his hand, the "Old Man" (as he was always called) stands looking at the works he loved so well. To one who sees this effigy daily, the thought often occurs: What would he think of them · now? grown even beyond his plans; and a certain amount of satisfaction is derived from the fact that during all this remarkable development the statue apparently stands constantly watching.

Although some years have now elapsed since his death, it is not possible for the country to gauge the value of his work by noting

the size or number of the factories which he was instrumental in creating. The full benefit accruing from it will not be separately assessable from national industrial progress; but for a generation to come England will have reason to remember Ludwig Mond, the great pioneer chemical manufacturer.   JOHN I. WATTS.

BENJAMIN HORATIO PAUL.*
BORN 1827; DIED 1917.

By the death of Benjamin Horatio Paul, in his ninetieth year, there is removed one of the last of the Olympians of the early epical years of British scientific pharmacy. His life pilgrimage, so full of years and honour, was for a long space of its course contemporaneous with the history and progress of the Pharmaceutical Society, to the faithful and fruitful service of which he dedicated so rich a measure of his remarkable talents and energies. The late Dr. Paul was born in 1827, and in his fourteenth year entered the profession of pharmacy at Fakenham. He was one of the group of eight students in the Pharmaceutical Society's original laboratory during the first session of the School of Pharmacy, and in 1845, at the age of eighteen, won the school's first prize in chemistry and the second prize in organic chemistry. While a student in the school he came under the inspiring and formative influence of Pereira, that prince of teachers and master in pharmaceutical science and lore, with whom he formed a life-long friendship, and whose memory he cherished as one of his most precious possessions. Thereafter he studied at Giessen, under Liebig, and in 1848 took the degree of Ph.D. (Giessen). Returning to England, he prosecuted his studies under Graham (the Master of the Mint), acting as one of his assistants, and passed the Major Examination in 1852, the number of his Major certificate being 9. He first contributed to *The Pharmaceutical Journal* in 1846, and in 1856 commenced a notable monthly series of articles on "The Progress of Chemical and Physical Science," which succinctly and with characteristic accuracy summarised and reviewed the advances in these branches of knowledge. He was soon recognised as a leading authority on the pharmaceutical and allied sciences, to the advancement of which his original work then and later materially contributed. In particular, his researches in collaboration with Cownley on the chemistry of cinchona, ipecacuanha, and other alkaloidal drugs, have made permanent additions to the knowledge of these subjects, and his literary labours, which covered a wide scientific range, included contributions to the first edition

* Reprinted, by permission, from *The Pharmaceutical Journal.*

of Watts's "Dictionary of Chemistry," editorship of the English version of the German edition of Payen's "Précis de Chemie Industrielle" (1878), for which he wrote the supplementary chapters on the chemistry of the metals; the editorship for Bohn's series of Bolley's "Manual of Technical Analysis"; the Report, in collaboration with Passmore, of the First International Exhibition at Vienna in 1883; and, in conjunction with Holmes and Passmore, the Report on the Materia Medica Pharmaceutical and Chemical Industry Exhibits at the Paris Exhibition of 1878.

Dr. Paul was formally installed as Editor of *The Pharmaceutical Journal* in 1870, in succession to Bentley, Redwood, and Barnard, the triumvirate who had conducted it with somewhat divided counsels and policy from the time of Jacob Bell's death in 1859. From the outset of Paul's editorship the *Journal* became a weekly, and he soon introduced many of the distinctive features that it retained during the thirty-two years of his tenure of office, which witnessed many profound and pervasive changes in the internal structure and external environment of pharmacy, and consequently in the policy of the official organ of the Pharmaceutical Society. Some of these innovations were doubtless distasteful to a man who had breathed the atmosphere and been nourished on the generous aspirations and exalted ideals of the morning land of British pharmacy; and, for one of his perfervid intensity of conviction, it must have been increasingly difficult to subdue his mind and hand to a medium in which science had to compromise with business. He scorned, however, to palter with principle, as he conceived it, and during his long life, both in his editorial capacity and later, he staunchly and steadfastly held out for the prime necessity of the systematic and progressive education of the pharmacist as the only sound basis and sanction for his claim to professional recognition, and insisted on the practical value of a regular apprenticeship, as alike a preventive and cure of many of the more grievous evils from which British pharmacy suffers. In these respects the recent trend of events has amply justified his prescience.

Dr. Paul was an accomplished and versatile linguist, widely travelled, with an intimate knowledge of Continental life and thought, a brilliant conversationalist, an artistic *raconteur* of remarkable histrionic power, with a wonderful gift of playful or poignant wit, and was cast in the heroic, combative mould, with elements of sweetness and light in his composition which made him one of the most chivalrous and magnanimous of men, as ready to take a manly foeman to his arms as to break a lance with him. Dr. Paul touched life on many sides. His affinities with the modern spirit in literature and art brought him into sympathetic contact

o*

and close communication with Dante Gabriel Rossetti and the protagonists of the pre-Raphaelite brotherhood, and Freemasonry as another aspect and manifestation of fraternity and fellowship strongly attracted him.

When Dr. Paul resigned the editorship of *The Pharmaceutical Journal* in 1902, although reckoned by the efflux of time he had exceeded the allotted span, he was still a man of vibrant vitality and unquenched spirit, and throughout his declining years had enjoyed wonderfully good health and an unabated zest of life.

RUFUS DANIEL PULLAR.

BORN JULY 6TH, 1861; DIED SEPTEMBER 22ND, 1917.

RUFUS DANIEL PULLAR was the elder of the two sons of the late Sir Robert Pullar. Born in Perth in 1861, he was educated, first at Sharp's Institute, Perth, and then at Craigmont School, Edinburgh. While still residing at Craigmont, he commenced to study chemistry at the University under Professors Crum Brown and Stevenson MacAdam. Here he made good progress, and at the completion of the course spent a year at his father's works in order to acquire a knowledge of practical dyeing.

In 1880 young Pullar entered the newly-created dyeing department of the Yorkshire College, now the University of Leeds, then in charge of the late Professor Hummel, with whom, indeed, he took up residence. He proved himself a hard-working and zealous student, and the University records state that he not only took the first prize and certificate in chemistry and dyeing, but also the highest honours and silver medal at the examination of the City and Guilds of London Institute in wool dyeing.

During the period of his stay in Leeds his kind and genial disposition found him many friends, and he enthusiastically entered into such sports as were then in vogue, being especially proficient in lawn tennis. He was, moreover, a clever photographer, and many prints are still extant from negatives taken by him during his year of studentship at Leeds. His interest in his old College and the subsequent phases of its development as part of the Victoria University and later as the University of Leeds, remained with him up to his death, and it was rarely he came to Leeds without visiting its dyeing department, so that he might discuss not only novel points of scientific interest, but also the possibility of methods for improving the study of his subject. His election in 1909 as a member of the Leeds University Textile and Dyeing Committee gave him much pleasure, and he often regretted that circumstances did not permit of his more frequent presence at its deliberations. It

was in 1882 that he took up the position of chemist to his father's firm, Messrs. J. J. Pullar and Sons, and now his real business career began. This well-known works was founded in 1824 by his grandfather, James Pullar, but its great development took place after 1848, when Robert Pullar, afterwards Sir Robert, became a partner. As chief chemist, Rufus Pullar continued until 1886, when he was received into partnership, and from that time forward his energies were so fully occupied in the development and enlargement of the business that his opportunities for actual chemical experiment became more and more limited. On the othe hand, his powers of organisation now came fully into play, and realising as he did the necessity of scientific methods, he spared no pains that these should be extended as far as possible throughout the factory. To further this object he visited foreign dye-works both in Germany, France, and America, and to these he had ready access, as a result of old family friendships which had originated with his grandfather. From its inception his firm, indeed, had closely watched each step in the advancement of the art of dyeing, and it was in these works at Perth that young Perkin, in conjunction with Robert Pullar, carried out the first experiments on any scale as to the application of mauve to fabrics. There are still in existence specimens of silk dyed with mauve at or about that time, much valued by both families, taken from a dress-length of heavy moiré silk which was presented to and graciously accepted by Queen Victoria.

As early as 1880 Pullar was elected a Fellow of our Society, and in the same year joined the Society of Chemical Industry. In 1883 he became a member of the British Association, at the meetings of which he was frequently present, and he indeed accompanied his father and uncle on its visit to Canada and the United States. His connexion with the Society of Dyers and Colourists dates from 1884, and of this in 1914 he became President, a position which he filled with distinction for two years.

From 1895 onwards Sir Robert and Mr. James Pullar, the older members of the firm, gradually withdrew from the actual management of the business, and as a result Rufus Pullar's active participation in scientific meetings, at no time an easy matter for him, owing to the distance of his home from their centres, was now considerably curtailed. Happy though he was in his own business sphere, in which, of necessity, his main interest centred, he never appeared better pleased than when in scientific circles; and there can be little doubt that he regretted that the exigencies of his position did not permit him actively to investigate some at least of the many theoretical problems which so frequently came to his notice. Whenever opportunity occurred, he spared no pains to emphasise the necessity

of a thorough scientific training for all those who were desirous of, or about to accept, positions of any responsibility in our factories, for, knowing the German methods so well as he did, he viewed with alarm the general neglect and lack of enthusiasm for science in this country. This was the tenor of his address to the Society of Dyers and Colourists in 1914, on which occasion he also pointed out that the chemist, to be thoroughly successful, should not specialise entirely in his own science, but should have also a general acquaint-ance with physics, engineering, and mathematics.   In 1914 he accepted with much pleasure the invitation to join the Board of Trade Committee, then being formed to consider the methods of improving the dye industry in this country, and when, as a result of its deliberations, British Dyes, Limited, was founded, his interest in the matter was unceasing, and at times he visited the factory site to watch the developments there in progress.

As the head of the large and important business at Perth, Rufus Pullar was fully alive to his many responsibilities, and in addition to his desire for the continued success of the works, was keenly anxious, as, indeed, were his father and uncle before him, to devise methods for the greater comfort and social betterment of the firm's employees.   Thoroughly businesslike and punctual in his habits, he expected the same from others, but, on the other hand, no calls on his leisure moments did he regret when these could be spent for the benefit of the community of his native town.   Even with those who knew him intimately he rarely discussed his own concerns, and his quiet and unassuming manner gave little indication of his excep-tional activity.

Although his business engagements were very exacting and his scientific interests absorbing, there are few, if any, of the numerous philanthropic institutions existing in Perth with which he had not been connected, either as president or in some position of active responsibility.   He had always, indeed, been particularly attracted by public work, and he had hoped later on, as others came forward who could relieve him of his business cares, to devote himself to public life and, if possible, to enter Parliament.

At the outbreak of the war he fully recognised the necessities of the situation, and actively participated in the various local schemes which arose at this period of the national difficulty.   Thus, when Lord Derby's recruiting scheme was started in 1915 he became a member of the Perth Advisory Committee, and this position he filled until March, 1916, when he was transferred to the Perth Appeal Tribunal.   Later again, in 1917, he agreed to become the Sub-Commissioner for Industry in Perthshire, under the National Service scheme, the duties of which, arduous though they were, he took up with much enthusiasm, and was bitterly disappointed when,

as time went on, this movement proved a failure. In 1916 he assisted in the formation of "The Association of British Chemical Manufacturers," and although not a manufacturer himself, ultimately became a member of its Council. It is probable that the frequent journeys to London in connexion with this and the Association of Chemical Industry, together with the worry involved by the troublous crisis which had arisen in his own factory, overtaxed his strength.

He died in Edinburgh on September 22nd, 1917, after a short illness at the early age of fifty-six years.

Mr. Rufus Pullar married a daughter of the late Robert Morison, of Perth, who survives him. He leaves two sons, Mr. R. Morison Pullar, who is director and secretary of the firm, and Captain J. Lindsay Pullar, of "The Black Watch," who is serving in France.

<div align="right">A. G. PERKIN.</div>

WILLIAM JAMES RUSSELL.

BORN MAY 20TH, 1830; DIED NOVEMBER 12TH, 1909.

IT is practically impossible to convey to a new generation any satisfactory impression of those features of a man's character and personality which were most apparent to his contemporaries. Hence it is of little use, and only for the satisfaction of those contemporaries, a rapidly dwindling company, that any reference is made to his genial presence, his characteristic hearty laugh, his sober and trustworthy judgment in business, and his quiet but persistent interest in matters scientific. Who he was and what he did can fortunately be set down with considerable accuracy and completeness, for documents remain which give all the necessary information. Few who knew Dr. Russell would have thought him likely to be one of those who not only made entries in a diary for the purpose of keeping engagements, but who set down every event in his own career from the age of fifteen to within a week of his death, and that all these memoranda should have been preserved.

William James Russell was born in May, 1830, and enjoyed the advantage of living under the care of father and mother during the whole of his early life, and therefore, although there is no record of his childhood, it seems certain that he received an enlightened kind of education. He went to two private schools, namely, Dr. Wreford's at Bristol and afterwards the Rev. Samuel Bache's at Birmingham. At this time, some idea of choosing for him the profession of engineering seems to have been introduced into the mind of his parents by several friends, and it was even

suggested that he should go as pupil to Mr. Beamish, a railway engineer. His father having been a good deal in Paris, had in 1801—3 attended the lectures of eminent men of science, particularly of the chemist Vauquelin, and it seems probable that the display of his interest in such subjects may have led the boy to think of the serious pursuit of chemistry as a life-long occupation. Moreover, he may have been influenced to some extent by tradition in the family concerning his father's, and especially his grandfather's, association with the famous discoverer of oxygen, Joseph Priestley.   Whatever may have been the original source of the influence which ultimately determined his career, the diary reveals the fact that at the age of fifteen or thereabout he was not only attending various lectures on geology, botany, and chemistry, but was lecturing himself either to schoolfellows or friends, probably the latter, as the entries appear to have been made in the holidays. On September 23rd, 1847, the entry is "Left Birmingham for good," and on October 13th following, "Came to London," and next day, "Began to attend the classes." This was at University College, London, where he became a student of chemistry under Graham and Williamson.

Though doubtless a man's career is subject to much modification by the conditions surrounding his life, there is at least as much to be attributed to the bias which he receives from his ancestry; and before proceeding further, a glance may be appropriately taken at the history of the strange and eventful lives of his father and grandfather long before his birth. This has been provided in an interesting volume, "The Russells of Birmingham in the French Revolution and in America, 1791—1814," by S. H. Jeyes (George Allen and Co., 1911), which has been compiled from letters and especially from the diaries kept by Martha Russell, elder of the two aunts of William James.

Russell's grandfather, William Russell (1740—1818), was a contemporary and friend of Joseph Priestley, the famous divine and discoverer of oxygen. At the time of this discovery, William Russell was thirty-seven years of age, and must have felt considerable curiosity about his friend's work and its results, especially as, in a sort of way as guardian and warden of the Assay Office in Birmingham, he was presumably acquainted with some applications of such practical chemistry as were known in his day. But the tie of sympathy between the two men was rather political and religious, Russell being a member of the Unitarian congregation presided over by Priestley, and a substantial supporter of the minister, not only as a member of his congregation, but by furnishing liberal supplies of money.   This association with so notorious a reformer, for

whom the High Church party of the day had no better name than "atheist" and "revolutionary," led to unfortunate consequences.

Public feeling in this country was exacerbated to a high degree by the outbreak of the French Revolution, and a series of disorders broke out in Birmingham, in the course of which Priestley's house was burnt and all his apparatus destroyed on July 14th, 1791, and the house of William Russell at Showell Green met with the same fate two days later. Priestley fled to London, and in April, 1794, he sailed for America and settled at Northumberland, a small town in Pennsylvania, where he died in February, 1804.

William Russell, though evidently a man of considerable courage and determination, having more than once confronted the rioters with remonstrances, was ultimately induced to seek a new home across the Atlantic. The story of the adventures of the father with his two daughters Martha and Mary and his son Thomas Pougher is recorded in the diaries of the elder daughter. To the volume already mentioned the reader must be referred for details, which, it must be said, possess more than a mere personal interest, as they throw much light on the state of parties in this country, on the condition of France during the Revolution, and on the social conditions prevailing in America. It is sufficient to say here that William Russell and his family started from Gloucestershire in July, 1794, and drove to Falmouth, where on August 13th they embarked. They had been at sea only a few days when they encountered a French frigate, and all the English voyagers were captured and taken to Brest. After some months they were released, and made their way to Paris, where they stayed until the following summer, when they sailed from Havre, and ultimately landed in New York in August, 1795. William Russell, ardent Republican though he was, found little to satisfy him in America, and in a few years the whole family returned to Europe.

Thomas Pougher Russell, the only son of William Russell, born February 3rd, 1775, was some years younger than his sisters, who were born respectively in 1766 and 1768. He seems to have found life in the new country less tolerable than did his more accommodating sisters. His father had purchased considerable property in France, and in 1801 he retired to his estate near Caen. Thomas spent a good deal of time in Paris, but there were difficulties about personal intercourse between father and son owing to the continuance of the war and the anomalous political position of the father. William Russell was admitted to the rights of French citizenship in 1807, and two years later Thomas also became a French citizen.

In 1813 Russell sold part of his French property, and advantage was taken of the peace which temporarily followed the internment

of Buonaparte in Elba for both father and son to return to their native country. No record exists of the terms on which Russell made his peace with the English authorities, but it is pleasant to know that he was spared to live four years in his native land. On January 26th, 1818, he died at the house of his son-in-law, James Skey, at Upton-on-Severn, aged seventy-eight, "a long suffering man who had met all his troubles with a cheery spirit and indomitable courage."

From the volume referred to, we learn that Thomas Pougher Russell maried in May, 1817, Mary, daughter of James Skey by his second wife, Eleanor (née Brockhurst), and had issue two daughters and one son, named after his two grandfathers William James. For the last thirty years of his life Thomas Russell was a banker in Gloucester, in partnership with James Skey and others. This private bank afterwards became the Gloucestershire Banking Company, of which he was a director. He also served for many years on the committee of the Gloucester and Berkeley Canal, and died in 1851 at Gloucester, of which city both he and his son were freemen.

As a student in University College, young Russell had the advantage of working under the most distinguished chemists of his time and of meeting with congenial companionship. Thomas Graham was the professor until his retirement on becoming Master of the Mint in 1855. At this time he was occupied with his famous studies of the phenomena of liquid diffusion. George Fownes was still professor of practical chemistry, but he died in January, 1849, and was succeeded by Alexander Williamson in October of that year. Russell's diary states that he began quantitative analysis in January, 1848, doubtless under the direction of Fownes, but as the diaries are missing for above a year at this time, there is no record of his associations with that brilliant man. On April 30th, 1850, "Heard that I had the medal for the Chemical Essay" is 'the entry. Other notes show that he went to hear Faraday lecture, and that on May 6th, 1850, he "went with Mr. Watts * to the Chemical Society to hear the discussion between Frankland and Hofmann about ethyl, amyl, etc."

Russell was not content with listening to discussions, for on the 29th of the same month, "Had a discussion at the Birkbeck Phil. Soc. whether Priestley or Scheele was the greatest philosopher. I spoke for Scheele; discussion adjourned.", And again, in November, "Opened the discussion on the Dr.'s new theory of etherification at the Birkbeck Philosophical Soc." But all was not science and work, for there are many entries of dances and

* Henry Watts of Dictionary fame.

dinners, and especially of visits to theatres; among the last,
November 11th, 1850, "Went with Frank and Henry Roscoe to
the Olympic Theatre to see Miss Faucit," etc. This was the end
of his student time at University College, for in January, 1851,
Frankland, who was then at the College of Engineering at Putney,
offered him the post of assistant at Owens College, Manchester,
then about to be opened, and where Frankland had been appointed
the first professor of chemistry. On February 8th, 1851, his father
died, and naturally this event took him away from his work for a
time; but by the end of the month he was in Manchester assisting
Frankland with his lectures, the introductory lecture being given
on March 20th. Here Russell remained until 1853, when he
decided to go to Germany.

July 1st: "The laboratory students met and presented me with
a copy of Tennyson's works as a parting gift, a most pleasing and
unexpected thing to me."

The choice of the laboratory at Heidelberg, where Bunsen was
professor, was determined on before the end of the previous year,
for a letter from Roscoe dated December 14th, 1852, contains the
following passage: "I am glad that you think of Heidelberg first,
because I have a great desire to go there too, and I am sure Bunsen
must be a capital man." Early in September Russell arrived at
Heidelberg, and on the 7th "Harry Roscoe and I went to see the
laboratory, a curious old place very different from the Owens College
one." Among his fellow-students were, besides Roscoe, Ronalds
and Matthiessen, Lothar Meyer, Edmund Atkinson, Pauli, Her-
mann, and Meidinger. Experiments on paraffin, which he had
begun at University College, weré carried on for a time, but soon
Bunsen suggested other work, and on December 16th, 1854, the
diary reports, "Took my degree." Whether the subject of his
thesis was the composition of the gases produced in flames or the
research on a method of estimating sulphur in volatile compounds
(published in the *Quart. Journ. Chem. Soc.*, 1854, **7**, 212) is un-
certain. He seems to have remained at Heidelberg until the
following August, when he returned to London.

After various disappointments and tentative experiments in
connexion with industrial applications of chemistry, Russell became
teacher at the Midland Institute, Birmingham, and gave a short
course of lectures in June, 1857. This summer the professorship
at Owens College, Manchester, fell vacant by the removal of Frank-
land to London. Russell became a candidate, but his friend Henry
Roscoe, his senior by three years, received the appointment.
Russell returned at the end of the year to University College, and
on December 7th "went to the laboratory, saw Williamson, and

he explained his gas apparatus to me; the thing is altogether in an impracticable form." This, however, was followed by a long investigation, which resulted in two papers jointly with Dr. Williamson (*Proc. Roy. Soc.*, **9**, 218; *Journ. Chem. Soc.*, 1865, **18**, 238), and two others independently, on gas analysis and on the application of the measurement of gases to quantitative analysis (*Journ. Chem. Soc.*, 1868, **21**, 128, 310). While this work in the laboratory was going on, Russell conducted the evening classes in chemistry at the college, and gave a course of practical chemistry in the school. During the first session of the Albert Veterinary College, he gave the course of lectures on chemistry, and in July, 1860, was appointed lecturer on natural philosophy at the College for Ladies, Bedford Square (Bedford College). He was now pretty fully occupied with teaching, but it did not prevent activity in other directions. He had attended several meetings of the British Association, and at the Oxford meeting in 1860 Russell took a lead- ing part in the foundation of the famous dining club, known as the "Bs." An interesting account of some of its proceedings was given in Dr. Scott's Presidential Address, March, 1916 (T., **109**, 342). The diary tells us that the rules of the club were drawn up on July 23rd, "the first meeting of our dining society" was on November 6th, and another meeting took place at the Cheshire Cheese on December 4th.

In October, 1861, Russell became engaged to Fanny Follett Osler,[*] a daughter of Abraham Follett Osler, the well-known glass manufacturer, of Birmingham. They were married on August 21st following, and took up their abode at 8, Circus Road, St. John's Wood. In 1865 he was appointed lecturer at the Royal Albert Veterinary College, and in the following February he bought the house 34, Upper Hamilton Terrace, which remained his London home to the end.

In 1868 Russell was appointed to the post of lecturer at St. Mary's Hospital, previously occupied by Matthiessen, and his activity may be estimated by recalling the facts that during the seven or eight years immediately previous to this time he had continued his teaching at University College and at Bedford College. He also attended meetings of the British Association, and on the last two occasions had served as one of the secretaries of the Chemical Section. He worked assiduously at gas analysis, and in conjunction with Williamson published several papers on the subject in the Proceedings of the Royal Society and in the Journal of the Chemical Society. He had also investigated jointly with Matthiessen the important question as to the cause of the

---

[*] She died on May 15th, 1871, leaving a son and a daughter.

vesicular structure of copper. They showed that this phenomenon is observed when copper is melted under charcoal only when oxygen or air is passed through the metal, and they inferred that the peculiar structure could only be attributed to the formation of carbonic oxide arising from the reduction of cuprous oxide within the mass by charcoal. The cavities in the metal are always untarnished, and hence cannot contain any oxidising gas. In 1863 he had communicated to the Chemical Society some important work on the atomic weights of cobalt and nickel, and was led to the conclusion that they are practically identical, the value found for Co′ being 29·370, whilst that for Ni′ was 29·369. The method consisted in the reduction of the protoxides by hydrogen and determination of the weight of the resulting metal. In 1869 he published further experiments, in which the same metal used in the former work was dissolved in dilute hydrochloric acid, and the evolved hydrogen was measured. The results were practically the same, and the atomic weights of the two metals were consequently supposed to be represented by the same number, namely, 29·3 or thereabouts. This was in accord with the view prevalent fifty years ago, even after the discovery of the periodic law. The problem presented by these two closely allied elements, however, attracted a large number of chemists, and the idea of the identity of their atomic weights has had to be abandoned. This may perhaps be partly attributed to advance of knowledge as to the properties of the two elements, including the discovery of nickel carbonyl, the decomposition of which affords a means of separating that metal completely from all other substances. There can be no doubt now that the atomic weight of cobalt is greater than that of nickel, and practically in the ratio given in the International Table of Atomic Weights, namely, Co:Ni::58·97:58·68, when O = 16. These values agree with the result obtained by comparing the specific heats, namely, 59·01:58·70. At St. Mary's Hospital, Russell remained about two years, but in December, 1870, he was appointed to the lectureship at St. Bartholomew's, left vacant by the unhappy death of his friend Matthiessen. A new laboratory had been very recently built and had been ready for occupation at the commencement of the session in October. Here Russell continued his work until he retired from all teaching in 1897.

A word may here be said on the subject of Russell's qualities as a teacher. He was wise enough to perceive that the course of elementary chemistry usually followed was unsuitable for medical students without modification, and the change he introduced undoubtedly affected the course of instruction in other medical schools

and the syllabuses of examinations, such as those of the Conjoint Board. All this led to great improvement in the attitude of the students of medicine toward the chemical subjects, for whereas there had been previously not only reluctance to attend, but frequent disorder, they soon recognised the sympathy of their present teacher, and there was little, if any, trouble during his connexion with the school. The diary gives evidence on this point, for on January 11th, 1871, the entry is: "Gave my first lecture at Bartholomew's; went off all right," and on the 14th: "Lectured again; students perfectly quiet." As to other difficulties consequent on the many changes which about that time arose not only in the requirements of the medical curriculum, but also in the working of the School itself, we have the testimony of Dr. Samuel West, who was then working in the laboratory with Russell, that they were met "with invariable good humour, willingness, and courtesy." He seized the opportunity of becoming President of the Chemical Society to deliver in 1890 an address setting forth his views on the teaching of chemistry to students of medicine. These were inspired with his characteristic good sense. But it was not only in relation to medical students that his interest and sympathy were engaged. He had great experience as a teacher of elementary chemistry and physics to young people, both at University College School and at Bedford College, and after retirement from the lectureship at the latter institution he became chairman of the Council and took an active interest in the development of the College. Part of his success as a teacher and examiner probably arose from the habit of his mind, which was more attracted by facts and phenomena than by theories concerning them. He was certainly not one of those who delight in the manufacture of hypotheses, and all his own work and teaching were directed by unaffected good sense and clear judgment.

In 1872 Russell was elected F.R.S. He was elected into the Royal Society Club on June 26th, 1879. In 1873 he was president of the Chemical Section of the British Association at Bradford. His address was chiefly devoted to the very appropriate subject of alizarin, the history of the discovery of its constitution, and of the then recent synthetical production of this important colouring matter.

The *Journal* of the Chemical Society contains, in January, 1874, a very interesting paper on the action of hydrogen on silver nitrate, in which it is shown that hydrogen passed into a silver nitrate solution causes the deposition of metallic silver in quantity equivalent to the hydrogen which is absorbed, provided the solution is prevented from becoming acid by introducing a small quantity of silver

ide. If the liquid becomes acid in consequence of the displace-
ent of the silver, nitrous acid is formed and the reaction becomes
ore complicated.

About the same time experiments had been going on in his
aboratory on a method of estimating urea in urine for clinical
urposes, and in August, 1874, the *Journal* contains a paper on the
ubject published jointly with Dr. S. West. The method was based
on the action of hypobromite on the fluid and measurement of the
evolved gases. This was followed up in the wards of the hospital,
and in 1880 the authors published their results in the *Proceedings*
of the Royal Society (No. 204, 1880).

Various other researches were carried on, and at the same time
Russell became involved in several technical inquiries which took
up practically all his spare time. In 1875 he was also appointed
one of the examiners in chemistry to the University of London.
His colleague for some time was Roscoe, and naturally the London
man got his full share of the work and the attendances at examiners'
meetings. In 1876, also, the movement began within the Chemical
Society which resulted in the formation of the Institute of Chem-
istry, and Russell's attendance at several initiatory meetings is
recorded in the diaries. He became president of the Institute in
1893, and served for three years. About this time the subject of
absorption spectra attracted his attention, and he spent much time
working with Professor Lockyer at South Kensington. The result
was a paper in the *Proceedings* of the Royal Society, 1880, on the
absorption spectra of cobalt salts. But more important results were
published (in conjunction with W. Lapraik) the next year on
"Absorption Bands in the Visible Spectrum produced by Certain
Colourless Liquids." Hartley and Huntington had already studied
the absorption in the ultra-violet (*Proc. Roy. Soc.*, 1880, **28**, 233),
whilst Abney and Festing had observed the absorption in the infra-
red end of the spectrum produced by colourless liquids (*Proc.
Roy. Soc.*, 1881, **31**, 416), but the visible portion of the
spectrum had not previously been examined, and the discovery
of bands in this part of the spectrum produced by the alcohols
and colourless hydrocarbons has led to a vast amount of work
by others since that date. The study of absorption spectra
interested Russell very much, and there was another paper, also in
conjunction with Lapraik, in the *Journal* of the Chemical Society
(1882) on chlorophyll," but, as he himself stated, the expectations
which had been raised and the hopes entertained when absorption
spectra began to be studied were not then fulfilled; nor can it be
said that they have been since. This, however, cannot be regarded
as an argument against carrying on such investigations; rather the

contrary, for inability to deduce definite conclusions merely indi-
cates a state of imperfect knowledge.

All kinds of problems which possess a direct practical interest or
value always attracted Russell, and this led him to devote a great
deal of time to the examination of the air and rain of London.
St. Bartholomew's Hospital Report (Vol. XX.) contains a record
of work done in 1882–3 on the carbonic acid in London air, whilst
the Meteorological Office Report for August, 1885, gives the results
of a laborious inquiry into the nature and amount of the impurities,
solid and gaseous, in London air.

Another subject which occupied much· time and attention was
the study of the action of light on water-colours undertaken in con-
junction with Sir William Abney at the request of the Science and
Art Department in 1886. The first report was issued two years
later, and contains an elaborate scientific discussion of the nature
of colour and the constitution of various lights to which water-
colours are exposed, as well as the influence of moisture and air
and the extent of the chemical changes observed. The conclusions
to which the investigators came may be briefly summarised in the
statement that mineral colours are far more stable than vegetable
colours, that moisture and air together are essential to the produc-
tion of change, and that it is the blue and violet components of
white light which are chiefly concerned in bringing about fading
in the pigment. One of the difficulties of the inquiry arose from
the fact that one of the main objects of the investigation was to
ascertain what changes water-colours would be liable to if exposed
to usual indoor conditions during at least an ordinary working life-
time. Fortunately, twenty-six of the colours originally subject of
inquiry had been preserved by Mr. T. H. Russell in his father's
house, and in 1914 they were examined by himself and Mr. Edwin
Bale, R.I. The results of their examination are recorded in the
Journal of the Imperial Arts League, and have been reprinted in
the form of a pamphlet, which has been published by Messrs.
Winsor and Newton, Ltd., so that artists can select for themselves
the colours which are known to be the most durable.

An inquiry of cognate character was directed as to the state of
the Raffaelle Cartoons at South Kensington. This Russell reported
on in July, 1891. Ancient Egyptian pigments were also the subject
of a lecture he gave at the Royal Institution in March, 1893.

It is time, however, to refer to his long connexion with the Chemi-
cal Society, of which he was elected a Fellow on March 3rd, 1851
(before he was twenty-one years of age), and of which forty years
later he became president. Absence in Germany and at Manches-
ter sufficiently accounts for the fact that the diaries give no evi-

dence of his attendance at the meetings for several years after election, but from 1857 onward he seems to have attended frequently in every year without a break down to the year of his death. In 1863 he first joined the Council, and thereafter he was an active member of various committees connected with the Society. He was elected Treasurer in 1876, and held that office until elected President in 1890. The great event during his occupation of the chair was the celebration of the jubilee of the Society, in 1891. As President, Russell took the chair at the dinner on February 25th, 1891, and the occasion was distinguished by the presence of the Prime Minister, Lord Salisbury. The diary characteristically reported that " it went off very well."

A series of experiments undertaken with the object of repeating Becquerel's observations on the photographic effects produced by compounds of uranium resulted in the remarkable discovery that zinc and a number of other metals produce a similar effect. The first announcement of the fact appeared in the *Proceedings* of the Royal Society for 1897. And the prosecution of the work led to the further discovery that not only metals, but varnishes, printing ink, and a variety of organic substances share this property. The results were collected in a second paper, which formed the Bakerian Lecture for 1898. The effects were soon traced to the formation of hydrogen peroxide, and in March, 1899, a third paper was communicated to the Royal Society under the title "Hydrogen Peroxide as the Active Agent in producing Pictures on a Photographic Plate in the Dark." One remarkable point brought out in these experiments was the exceedingly minute quantity of the agent which was competent to produce the effect. The inquiry was pursued for some years, and the effects on a photographic plate produced by sections of various woods provided a fascinating subject, which was developed with many beautiful illustrations and communicated to the *Philosophical Transactions* for 1904. Two later papers described the effect produced by leaves and other parts of plants, also by resins. In 1897, Russell had resigned the office of lecturer at St. Bartholomew's Hospital, which he had held for so many years, and after this time his experimental work was done at the Davy-Faraday Laboratory. Here, also, he carried out the experiments on the "Formation of Definite Figures by the Deposition of Dust," which were published in the *Philosophical Transactions* for 1903. An explanation on physical principles of the formation of these curious deposits was soon afterwards given by Mr. J. Aitken, F.R.S. (*Proc. Roy. Soc.*, 1904, **72**, 211).

Russell was elected under Rule II a member of the Athenæum Club on February 26th, 1889. The rule provides for the annual

introduction of a small number of "persons of distinguished eminence in science, literature, or the arts, or for public services." A few years later Russell became a member of the Committee.

Russell delighted in the country and in all sorts of natural objects and in scenery. He had travelled a good deal on the Continent of Europe, but his own country supplied him with all the enjoyment he needed in his latter years. And he was a most genial host. For many years, from about 1882, he had a house on the edge of Dartmoor, Scorhill, near Chagford, and there he delighted to show his visitors the views of sunsets over the moor or the curiosities of form among the tors. Notwithstanding its attractions, the difficulty of access to this retreat led to a removal in 1897 to St. Ives, near Ringwood, Hants, a house surrounded by beautiful plantations, including extensive rhododendron avenues. Here he entertained frequent visitors, and the annual excursion into the neighbouring New Forest at Whitsuntide was an event for pleasant anticipation. It was delightful to accompany him in visiting his favourite trees in his own grounds, and to share the evident enjoyment with which he discoursed about their history or peculiarities.

In August, 1909, he left London as usual, and went to St. Ives. He had, however, been failing in physical strength for some time, and though in the early part of the summer he had dined out several times, there is an entry in the diary on July 18th, "Taken ill," and on August 10th, "Went to Ringwood." Here, after a short illness, during which he was unconscious, he passed quietly away.

W. A. T.

FRANCIS SUTTON.

BORN FEBRUARY 19TH, 1831; DIED APRIL 16TH, 1917.

THE name of Francis Sutton is known throughout the chemical world by reason of his authorship of "A Handbook of Volumetric Analysis," which has been recognised as the standard work on the subject for the past fifty years. Ten editions of the work were published during the author's life, and each edition has kept well abreast of the current work in this branch of analysis. Sutton contributed but little original matter to analytical chemistry; his strenuous life and professional engagements never allowed him time for development in this direction, although his natural ability and grasp of the science might, in other circumstances, have enabled him to become a great chemist.

Francis Sutton was an only son, born on February 19th, 1831, at

Great Plumstead, a village near Norwich, Norfolk. *His father,* Francis Sutton, was a small farmer and farrier with a local veterinary practice. The son received his earliest education at the village school of Blofield, two miles distant from his home, and later attended a private school in Norwich, riding daily the ten miles to and fro by pony.

At the age of fourteen young Sutton was placed with a Mr. Harper, a druggist, of Norwich, with a view to acquiring some knowledge of drugs and chemicals prior to being sent as a student to the Veterinary College in London, for his father intended the boy to become a veterinary surgeon. The study of materia medica, botany, and chemistry was found so interesting that with his father's consent he was apprenticed to Mr. Harper and remained with him as assistant until 1851.

Then, at the age of twenty, Sutton decided to join a former fellow-apprentice who had started a druggist's business in West Clayton Street, Newcastle-on-Tyne, and it is of interest that the journey to the northern town was made by sea in a small coasting vessel from the now dead port of Blakeney on the north Norfolk coast. Thus he was brought into contact with a then growing centre of chemical industry and study, and while practising pharmacy had opportunity of becoming acquainted with men interested in pure and applied chemistry, among others Joseph Wilson Swan and John Pattinson, who remained life-long friends. A Dr. Glover, a physician of Newcastle, who devoted a good deal of time to medical chemistry and analysis, and subsequently became physician to the Royal Free Hospital, London, took much interest in the young pharmacist of West Clayton Street, lending him books, employing him in various chemical experiments as an assistant, and advising him to take up seriously the study of scientific chemistry. As a result of this help and encouragement, Sutton, in such time as was available, attended the lectures and worked in the laboratory of Dr. Richardson, then lecturer in chemistry at the Newcastle College of Medicine—at that early date associated with the University of Durham, and later known as the University of Durham College of Medicine. It was, however, through Dr. Marreco, then assistant to Dr. Richardson, that he received his main instruction in the theory and practice of chemistry, and laid a firm and sure foundation for his subsequent interest and achievement in that science. He must have been an apt and earnest pupil, for, as junior partner in the druggist business, most of the day was fully occupied, and his lectures and laboratory work had to be snatched at odd hours.

His residence in Newcastle and the opportunity for instruction

came to an abrupt end in November, 1854. His old master at Norwich was dying, and an urgent appeal was made to Sutton to return to Norwich and manage the business in which he had served his apprenticeship. He did so, and settled in Norwich, carrying on the pharmaceutical business in partnership with his late master's widow, and subsequently alone, until growing interests necessitated taking a partner. Meanwhile his keen interest in chemistry and chemical analysis was maintained, and led to part of the business premises being converted into a laboratory. At this period the work of Lawes and Gilbert at Rothamsted in the use of artificial fertilisers was beginning to receive the attention of agriculturists, and Sutton turned to the study and analysis of fertilisers. By advocating the new ideas among local farmers and advising and helping them, he established the nucleus of an analytical and consulting practice, which quickly developed.

In 1870 he originated and became managing director and part-ner in a chemical manure works at Runham, Great Yarmouth (Baly, Sutton and Company, Ltd.), where the manufacture of sul-phuric acid, hydrochloric and other acids, as well as superphos-phates, chemical manures, and sulphate and chloride of ammonia was carried on. The works and business were disposed of in 1893 to Messrs. Prentice Brothers, Ltd., of Stowmarket.

While at Newcastle in 1853 Sutton had become a member of the Pharmaceutical Society, and in Norwich his ability as a pharmacist was quickly recognised. He was elected to the Council of the Pharmaceutical Society in 1870 and continued to serve until 1876, when he finally abandoned pharmacy and disposed of the business to his then partner—in order to devote his time to his consulting and analytical practice and other interests. While serving on the Council of the Pharmaceutical Society he was chosen as one of the two delegates to represent Great Britain at the International Phar-maceutical Congress in St. Petersburg in 1874, and was afterwards elected a corresponding member of the Imperial Pharmaceutical Society of that city and also of the Apotheker Verein of Vienna.

Sutton's earliest contribution to scientific literature was in the form of two papers, published in the *Chemical News* in 1860, on the volumetric determination of phosphoric acid by uranium. In 1862 the first edition of his "Volumetric Analysis" was published; it was a small volume of 273 pages; the second edition followed nine years later in 1871, and was much more ambitious and com-prehensive. Professor H. McLeod contributed a section on gas analysis, and the late Mr. William Thorp contributed to the section on water analysis. The latter, by advice and correction of proofs, gave acknowledged assistance in many subsequent editions.

The fourth edition was translated into French by the late Dr. C. Méhu and published in Paris in 1883. In all, ten editions were published in Sutton's lifetime, the last being edited by his son, W. Lincolne Sutton, and A. E. Johnson.

The period of life between 1860 and 1876 was an exceptionally full one, for Sutton, while carrying on simultaneously a very successful pharmaceutical business, had established and developed a considerable analytical and consulting practice, published the first and larger subsequent editions of his book, and had founded and was managing the chemical works at Yarmouth He had been appointed analyst and consulting chemist to the Norfolk Chamber of Agriculture, public analyst for the County of Norfolk and Borough of Great Yarmouth, and gas examiner to the City of Norwich. For many years he was in considerable demand as an expert witness before Parliamentary Committees and in the Law Courts.

Francis Sutton undoubtedly possessed great natural ability and versatility and had wide interests. In his prime he was a strikingly handsome man, with finely moulded head, aquiline nose, full beard, and ruddy complexion. His generous nature, sociability, and love of "good company" endeared him to a wide circle of friends; another personal trait was his beautiful handwriting. He took an active part and held office in various local scientific and other societies, such as the Norfolk and Norwich Geologists' and Microscopical Societies (both now extinct), the Norfolk and Norwich Naturalists' Society, of which he was at one time president, and he was an original member of the Norwich Science Gossip Club. He was a great lover of music, and possessed considerable knowledge of classical and operatic music. He was an active member of the Norwich Philharmonic Society for over forty years, and played the clarinet and later the oboe in the orchestra. He served for many years on the general committee and committee of management of the Norfolk and Norwich Triennial Festivals. He was an omnivorous reader of catholic taste, and served for many years on the committee of the Norfolk and Norwich Library, some time as president. Throughout his long life his chief outdoor recreation was fishing, a sport in which he took general interest. He was appointed a juror to the original Fisheries Exhibition held in Norwich in 1881 and also in the International Fisheries Exhibition of 1883 held in London.

Francis Sutton married in 1859 Marianne Harriett, the youngest and eleventh child of William Lincolne of Halesworth, Suffolk, and had issue seven children, three sons and four daughters, all of whom lived to maturity and married.　　　　　　　　　F. N. S.

WILLIAM HENRY SYMONS.

BORN NOVEMBER 16TH, 1854; DIED AUGUST 25TH, 1917.

THE ranks of the Public Health Official Service suffered the loss of a most capable and enthusiastic member by the death, on August 25th, 1917, of Dr. William Henry Symons, for twenty-one years Medical Officer of Health of the City of Bath.

Born on November 16th, 1854, Dr. Symons, a native of Dunster, first adopted chemistry as a vocation, and becoming chemist to Messrs. Idris and Co., aerated water manufacturers, of Camden Town, rapidly acquired a considerable practice as a consulting chemist. During this period he became a member of the Chemical Society in 1874, Fellow of the Institute of Chemistry in 1888, and published various papers, among them being: "A new method for the detection of various starches," "The detection of sodium in lithium carbonate," "Ulexine, an alkaloid from the common furze," "The difference between ulexine and cytisine," and a paper in the *Transactions* "On the volumetric determination of carbon dioxide in the atmosphere." His inclinations were, however, towards the application of chemistry to medicine, and entering St. Bartholomew's, he obtained the M.R.C.S. and L.R.C.P., and the M.D. Brussels in 1894, and the D.P.H. of Oxford and Durham in the following year. During this period he acted as assistant demonstrator in materia medica, was examiner under the Pharmacy Act, published papers on "Ipecacuanha," and edited the "Year Book of Pharmacy." For a short time he acted as Medical Officer of Health to St. George's, Southwark, and was appointed to the City of Bath in 1896. During the twenty-one years in which he held this post, he inaugurated a completely new régime with regard to the municipal health department, and his elaborate reports on the health of the city were greatly valued by the Corporation. His work in connexion with child welfare at Bath "brought this branch of public health work to a high standard of efficiency, and his efforts to secure a thoroughly satisfactory midwifery service in the city, embodying the provision of the Municipal Midwives Act, were fruitful of good results." For some years he was a member of the council of the Society of Medical Officers, and president of the West of England branch in 1911.

His interests were wide: he had made a special study of town planning, and in this connexion frequently visited the Continent; he also took an active part in the organisation of the Wensley Sanatorium, near Bath, for tuberculosis. One of his hobbies was

meteorology, and it was through his energy that the meteorological department at Bath was modernised, several stations equipped, and for the first time a series of careful observations recorded. This was obviously of value to a city famous as a health resort, and led to his appointment as City Meteorologist and a member of the Committee of the British Association appointed to investigate the effect of climate upon health and disease.

He was a well-known member and fellow of the Royal Sanitary Institute, and contributed to their *Journal* and discussions. Among his contributions, not previously mentioned, were the following: "Cancer in relation to the dwelling," "Ventilation," "The life-history of *Musca domestica*" (and it may be mentioned that he was a pioneer in the crusade against the fly danger), "Flies and refuse heaps," "Distribution of phthisis."

In the obituary notice in the *Journal* of the Royal Sanitary Institute, one of his friends wrote as follows: "One of his most striking personal qualities was his great enthusiasm in whatever he undertook . . . no one who was brought into intimate relationship with him ever harboured any unkindly sentiment towards him. The golden qualities which made him a model husband, father and friend, were somewhat cloaked by an excessive natural reserve, but these qualities were bountifully disclosed to many friends and colleagues who mourn his loss and who will be inspired by the memory of his friendship, and the earnest endeavour which secured for him the reward of much good work accomplished in the sphere of public health." F. F.

THOMAS TYRER.

BORN NOVEMBER 17TH, 1842; DIED FEBRUARY 21ST, 1918.

THE sudden death of Mr. Thomas Tyrer, which took place at his residence, 14, Sandswell Mansions, Hampstead, on Thursday, February 21st, is already generally known to the chemical world at large, and it came as a great shock to such intimate friends as the writer, who had the privilege of being one of his closest friends and was associated with him both in business and private life for some twenty-nine years.

Although of good age, there was a fair prospect of further years of useful life, but the death of Mrs. Tyrer and a recent operation for cataract evidently affected his health and tended to hasten the end.

As one who was treated by Mr. Tyrer as a son or younger brother, the writer feels that (beyond the great loss sustained by chemical industry) the world has lost a good man— one who was generous and good-hearted, always ready to acknow-ledge and help forward others, even at the expense of himself. Although somewhat hasty in temper (like many other great men), Mr. Tyrer never knowingly allowed his feelings to injure or hurt anyone, and as a friend and adviser would spare no trouble or expense to render the very best possible help, his help being by no means confined to those who could claim strong personal friend-ship. In business he was generous to all who in any way showed themselves faithful and earnest, and he had no sympathy with those who believed that in business the great and strong are justified in " ousting " the smaller and weaker man.

He was able quickly to grasp the salient points and master the details of any matter placed before him, and his sound reasoning and extensive and general knowledge made him a valuable coun-sellor, whilst he was also possessed of great diplomatic ability. Had he turned his thoughts towards political life he would doubtless have become one of the leading men in the government of the country

As has already been mentioned in the various trade journals Mr. Tyrer's connexion with commercial and industrial chemistry extended over some fifty-five years.   He was born at Wolver-hampton in 1842, and received his education from his father, who was a schoolmaster, from whom he also acquired his habit of fear-lessly speaking the truth to all and in all circumstances where necessary.

He was apprenticed to a manufacturing chemist named Wild-smith at the age of fifteen, and he entered the Royal College of Chemistry in Oxford Street (now incorporated in the Imperial College of Science) in 1861, and studied here under Hofmann, his experience with whom and with his fellow-students being always a favourite theme for conversation.

He also studied biology under Huxley and physics under Tyn-dall, but owing to the condition of his finances he had to relinquish these studies and became technical manager to Messrs. May and Baker, of Battersea, of which firm he subsequently became a partner.

Meanwhile, he was acting as honorary lecturer in chemistry to a working man's institute.   His partnership with Messrs. May and Baker terminating in 1889, he, on January 1st, 1890, acquired from Messrs. Dunn and Co. the Stirling Chemical Works, Strat-ford, which in 1898 was formed into a limited liability company

Thomas Tyrer and Co., Limited); of this he became managing
director, and held this position at the time of his death.

In 1912 he undertook the manufacture of cellon aeroplane dope,
and on the outbreak of war in 1914 he was able to extend and
keep pace with the demand. Later on, by the erection of one of
the best equipped factories, he added largely to the output, and
was able to cope with the continually increasing requirements of
the Government, due to the war.

Outside his business, some of the widest known work he did was
in connexion with the duty-free alcohol question and the founda-
tion of the Society of Chemical Industry. As chairman of the
Chemical Trade Section of the London Chamber of Commerce, he,
in conjunction with David Howard, Charles Umney, and others,
took part in obtaining the grant of duty-free spirit for medicinal
and other alcoholic preparations to be sent abroad, and thus enabled
English manufacturers to compete with the foreign trade in these
products.

He was also successful as a member of the Industrial Alcohol
Committee in obtaining the reduction of the quantity of wood
spirit used in denaturing alcohol (for use in manufacture) from
10 to 5 per cent.

In connexion with the Society of Chemical Industry, which was
really instituted by a meeting of chemists convened by Mr. Har-
graves at Widnes in 1879, and subsequent meetings at Widnes,
Liverpool, and Manchester (known first as the Widnes and Run-
corn Chemical Society, and later as the Lancashire Chemical Society
and the Society of Chemical Engineers), Mr. Tyrer was most active,
and may be said to have been one of its principal founders. In
April, 1881, a meeting was held at Burlington House, at which Mr.
Tyrer, with G. E. Davies, Roscoe, Abel, Ludwig Mond, Spiller,
and other famous chemists took a most prominent part, Mr. Tyrer
suggesting that the society be called the Society of Chemical Indus-
try, and this suggestion was adopted in spite of opposition. He was
honorary secretary of this society for ten years, chairman of the
London Section 1890—1892, president 1895—1896, and honorary
treasurer from 1908 (after the death of Mr. Hall) to the date of his
death.

During the whole time he served the council in every direction,
and his energies in this connexion aided materially in bringing the
society from a small beginning to one of the largest, the members
now numbering from four thousand to five thousand. That his
great efforts in the chemical industry were recognised is shown by
the fact that he had many honours conferred upon him, amongst

which may be mentioned the award of a silver salver and purse of gold by the Society of Chemical Industry under the presidency of Sir Fredk. Abel in 1891, the medal of the society in 1910, and in connexion with the industrial alcohol question a silver tea and coffee service in 1905.

One might go on indefinitely describing the work of such an energetic worker as Mr. Tyrer, but the greatest thing of all is the character he leaves behind, which cannot be better expressed than by quoting Professor Henderson's recent words.

"Kind-hearted and generous; a steadfast friend and chivalrous opponent; a wise and cautious counsellor; a benevolent helper of many a young and struggling man; an earnest advocate of every cause which he believed to be right and good; eminently sociable; a lover of music, a lover of talk in congenial company—such was Thomas Tyrer. It will be long before his memory fades."

Mr. Tyrer died as he wished, "in harness," and, as Professor Henderson says, it will be long ere his memory fades, especially amongst those who knew him well and recognised his real worth.

T. TUCKER.

REGINALD COWDELL WOODCOCK.

BORN DECEMBER 11TH, 1851; DIED JANUARY 5TH, 1918.

REGINALD COWDELL WOODCOCK received his early education at two private schools, and subsequently (1866–1867) attended King's College School, London, taking the regular course in French, German, drawing, chemical physics, etc.

During 1867–1868 he was employed in Paris by tne London Warming and Ventilating Co., assisting his father in a series of experiments in the Pantheon, preparatory to the introduction of heating the buildings by means of the "Gurney" stoves. He frequently visited Paris after that time, and was there when the Revolution broke out, followed by the removal of Napoleon III.

Having attended some lectures at the Royal College of Chemistry, he joined as a regular student in 1869, passing the examination in June, 1870, when he obtained a first class certificate and the "Special Certificate" for research work, "On the Action of Normal and Acid Salts upon Ammonium Salts, especially upon Ammonic Chloride," published in the *Journal of the Chemical Society*, 1871, **24**, 785, also in Watt's "Chemical Dictionary," 2nd Suppl., p. 60. In October, 1871, he became private assistant to Dr. Frankland at the Royal College of Chemistry, and was engaged in that capacity

on chemical analyses and research work, one lengthy investigation being for the Russian Government in respect of the destructive distillation of various woods and the possibilities of making use of the gases produced therefrom for illuminating purposes.

He was elected a Fellow of the Chemical Society in December, 1871. In January, 1872, he was appointed chemist to the Bede Metal and Chemical Co., Ltd., Jarrow-on-Tyne. In March, 1873, he received the appointment (following his friend, the writer) as assistant professor of chemistry at the Royal Agricultural College, Cirencester, where he remained until 1878. During his stay at Cirencester he conducted a considerable amount of research work for Professor A. H. Church in animal and vegetable chemistry, on turacin, a bird pigment from the Turaco, containing copper; colein, the colouring matter of the Coleus plant; vegetable albinism; aluminium in plants; eugenol; etc. Being registered as a teacher by the Science and Art Department, South Kensington, he gave a course of lectures at Cirencester in 1874 on inorganic chemistry. In 1878 he was elected a Fellow of the Institute of Chemistry. From 1878 to 1886, Woodcock was associated with the late G. W. Wigner and Messrs. Wigner and Harland, in their practice as analytical and consulting chemists and public analysts.

In 1886 he received an appointment with the American and Continental Sanitas Co., and accompanied the writer to New York, U.S.A., in order to start a factory and branch business in that country, remaining there until March, 1906, when he returned to England and joined the parent Sanitas Co., Ltd., in order to assist the writer in his charge of the chemical and bacteriological laboratories of the company, of which Mr. Woodcock subsequently became a director. During his stay in New York he was largely instrumental in initiating the New York section of the Society of Chemical Industry, and served as honorary treasurer from its formation, a farewell dinner being given to him by the members on March 24th, 1906. He also served as a Vice-President of the Chemists' Club, New York City. Ill-health caused him to resign active work with the "Sanitas" Co., Ltd., in March, 1916, but he remained on the board of directors up to the time of his death.

The research work in which he was engaged with the writer during this latter period of his career was very varied in character, and embraced the results covered by the following joint publications: "Bacteriological Testings of Certain Disinfectants, and the results as Affected by Varying Conditions." (Communicated to the British Pharmaceutical Conference, Cambridge, 1910. *Pharm. J.* 1910, **85**, 157). "The Bacterial Testings of Disinfectants. A Practical Criticism." (*Analyst*, May, 1913.) "The Production of

Formic Acid by the Atmospheric Oxidation of Turpentine." (*J. Soc. Chem. Ind.*, 1910, **29**, 791.) "The Production of Formic and Acetic Acids by the Atmospheric Oxidation of Turpentine." (*J. Soc. Chem. Ind.*, 1912, **31**, 265). "Some Experiments concerning Antiseptic Inhalations" (*J. Clinical Res.*, 1914, October.)

Mr. Woodcock was a member of the Society of Public Analysts, an original member of the Society of Chemical Industry, and served as a vice-president of that body for some years.

The writer first made the acquaintance of his late lamented friend in the rooms of the Chemical Society in the spring of 1872, and enjoyed unbroken friendship down to the time of his decease. Mr. Woodcock, if not a rapid worker in the laboratory, was most exact and painstaking—almost to a degree of fastidiousness—so that his work was always eminently trustworthy. He was of genial character, extremely well read, of the highest rectitude, and his loss will be deeply mourned by all who knew him at all intimately.

C. T. Kingzett.

PHILIP JOHN WORSLEY.

Born October 29th, 1834; Died March 7th, 1917.

Philip John, the son of Philip Worsley, was born in London and lived there during his school and college days. His taste for chemistry showed itself when he was quite young, and was encouraged by his grandfather, John Taylor, F.R.S., and his uncles, who were mining engineers. He entered the Junior School of University College, Gower Street, in September, 1843. In speaking of his school days, he said that he was not successful because he seldom kept his mind continuously on his work; classics did not come easily to him, and he had the greatest difficulty in learning by heart, but he was interested in chemistry However, he worked better when he went to University College in 1850, where he greatly appreciated the teaching of Augustus de Morgan in mathematics and of Thomas Graham in chemistry. He graduated in 1853 with honours in chemistry. Among his fellow-students were George du Maurier, Michael Foster, George Carey Foster, and George Buchanan. The great exhibition of 1851 brought many distinguished scientific foreigners to his grandfather's house in Kensington, which gave the young student of chemistry and prospective mining engineer opportunities of hearing discussion on all the latest discoveries and theories.

In 1853 he went with his uncle, Richard Taylor, on a visit to lead mines at Pontgibaud in the Auvergne, where he was given the run of the works. From Pontgibaud he went by coach to Marseilles, the railway not being opened beyond Lyons; here he

stayed with a great-uncle, Philip Taylor, who had engineering works, which have since become one of the shipbuilding yards of the French Navy—les Forges et Chantiers de la Méditerranée. His next experience was in Germany, where he went to be educated as a mining engineer at the Bergakademie, or Royal School of Mines, at Freiberg in Saxony. On the way he passed through Heidelberg, and was taken by his friend Henry, afterwards Sir Henry, Roscoe to see Bunsen's laboratory. Before attending lectures at the Bergakademie, the students had to take a practical course either in the mines or the smelting works; Worsley chose the latter. On his own initiative he made careful notes of the process accounts, giving the results and cost of the various operations, which were invaluable to him in later days. On his return from Germany in 1854 he took a course of practical chemistry in the Birkbeck Laboratory at University College, London, under Professor Alexander W. Williamson and Assistant Professor Henry Watts, author of the well-known "Dictionary of Chemistry."

In 1855 came his first employment. He was sent to Ireland to assist Dr. Gurlt, a former Freiberg student, in working a new process for extracting copper from poor ores for the Wicklow Copper Co. This only lasted for a month or two, his first regular work being at Rotherhithe, where he started works for Messrs. H. J. Enthoven and Sons for separating silver from lead, superintending the erection of the plant, and constructing subsidiary furnaces from his own plans. While here he joined the Chemical Society, being elected a Fellow on February 4th, 1858. He stayed at Rotherhithe until 1860, when he went to Bristol as assistant manager of the Netham Chemical Works.

In the autumn of 1856 his grandfather, who was treasurer and an original member of the British Association, took him to the meeting at Cheltenham and made him an associate. His friends of the Chemical Society put him upon the committee of Section B of the Chemical Section. It was at this meeting that Sir Henry Bessemer described his process of burning the carbon out of pig-iron, which was the first step towards the modern process of making Bessemer steel. In 1858 Philip J. Worsley and George Carey Foster went together to the meeting at Leeds, where they met the set of young chemists whom he had seen working in Bunsen's laboratory at Heidelberg in 1854. They did not appreciate the social evenings of the Association, but met in each other's rooms and formed what they called Sub-Section B; these meetings were full of fun and interest, and other friends besides the original members asked to be allowed to join them.

In 1860 the Chemical Works at Netham were a small affair with a capital of £15,000. They had been going for a year and a-half,

and were in a very bad way. The new young assistant manager was thrown entirely on his own resources; he knew the theory of the processes, but in practice all was new to him. He soon found that the business was not prospering, and that unless he could improve the manufacture it would soon come to an end. He gradually introduced improved methods and instituted a system of regular sampling and testing the various stages of the work. Common sense with theory as a guide soon began to tell, and the reign of chemical anarchy and muddle gave place to order and system. After three months of probation he was made manager. After a time Netham chemicals got a high repute and were in constantly increasing demand. The plant and capital were increased every few years, and the directors' appreciation of his management was shown by their giving him a place on the board in 1871.

In 1873 he joined with other alkali manufacturers to form the Bleach Association, at which he made the acquaintance of all the leading men of the trade, some of whom were already his friends or schoolfellows. At a later period, when the Netham Chemical Company was merged in the United Alkali Company (1890), he met many of them again and worked with them as a fellow-director, keeping his seat on the board until 1901.

As a young man, Worsley's strong inclination was towards pure science. He imagined that he would always be able to keep up his interest in chemistry, and that he might in his leisure find time to make investigations which would establish him as the equal of the men of science who were his friends. However, instead of working in a private laboratory, he gave his scanty leisure to the cause of education and philanthropy. From the chairmanship of the St. George's School Board (Netham is in the parish of St. George, Bristol) to the vice-chairmanship of the University College, afterwards the University of Bristol, he helped to forward every grade of education in the city. As a Liberal in politics and a Unitarian in religion, he took an active part in public life. His chief recreation in his later years was gardening, and one of his greatest pleasures was the success he obtained in producing new varieties of daffodils by hybridisation.

As a memorial of his great work in connexion with the University of Bristol and his interest in the chemical department, a gift has been made to the chemical library, the interest of which is to be used annually to make additions of books and periodicals. He had given the greater part of his private collection of books on chemistry to the University during his lifetime.   A. W.

Organic Chemistry.

Solubility of Lead Acetate in Water. YUKICHI OSAKA and REIJIRO HARA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 147—150).— Measurements have been made of the solubility of lead acetate in 0.025, 0.05, and $0.1N$-acetic acid at $25°$, $35°$, and $45°$. The quantity of salt dissolved per 100 grams of water increases slightly with the acidity of the solution, the relation being linear. By extrapolation, the solubility in pure water is found to be 54·38 parts per 100 of water at $25°$, 87·77 at $35°$, and 154·25 at $45°$. These extrapolated values are based on the assumption that the salt is not hydrolysed.   H. M. D.

Physical Properties of a Number of Pure Esters. J. HOWARD MATTHEWS and KATHARINE E. FAVILLE (*J. Physical Chem.*, 1918, **22**, 1—21).—The esters, obtained from Kahlbaum, were purified by chemical treatment according to the method described by Young and Thomas (T., 1893, **63**, 1191), and then subjected to fractional distillation in an apparatus devised to give a constant pressure of 760 mm. In accordance with the results obtained by most of the previous observers, the boiling points of the esters were found to extend over an appreciable range. The physical properties measured were the boiling point, density, viscosity, specific inductive capacity, and refractive index, the values being recorded in the table.

	B. p.	D_4^{20}.	$\eta_{20°}$.	$\varepsilon_{20°}$.	n_D.
*iso*Amyl formate	123·46²—123·56⁵	0·8773	0·789	4·98	1·39772
*iso*Butyl formate	98·15 — 98·25	0·8832	0·638	5·93	1·38568
Propyl acetate	101·57 —101·77	0·8869	0·585	8·10	1·38422
Ethyl propionate	99·12 — 99·22	0·8904	0·545	5·75	1·38414
Propyl propionate	121·0 —121·25	0·8809	0·674	4·66	1·39325
Ethyl butyrate	120·0 —120·5	0·8784	0·665	5·91	1·40002
*iso*Butyl valerate	167·0 —168·5	0·8544	1·118	8·21	1·40569

The boiling points of the esters at various pressures were also determined, and the results applied in testing the deductions made by van der Waals in reference to the theory of corresponding states. For ethyl propionate, ethyl butyrate, and *iso*butyl formate, critical data have been previously determined, and by making use of these a comparison is made of the values of the ratios of the absolute temperatures at corresponding pressures to the absolute critical temperatures. For a given pressure, the temperature ratio varies appreciably with the nature of the ester, but the deviations from constancy are less than those found by Young and Thomas in their investigation of a series of ten esters.   H. M. D.

Relation between the Affinity Values of the Aliphatic Acids of the Mono- and Di-basic Series. GERVAIS LE BAS (*Chem. News*, 1918, **117**, 121—122).—Tables of the affinity values ($k \times 10^4$)

of monobasic fatty acids, starting with formic acid, and of dibasic fatty acids, starting with succinic acid, are given. The latter form a nearly arithmetical series, that is, the values for $n(k \times 10^4)$, where n represents the position in the series, are very nearly the same. If the numbers for the members of the dicarboxylic acid series be divided by the numbers for the members of the monocarboxylic acid series, a series of numbers is obtained which, when plotted against successive integers, gives a curve resembling a rectangular hyperbola. The free energy due to the carboxylic group in the monobasic acid series diminishes with the increase in the length of the hydrocarbon chain. When two such groups are present in the same molecule the ratio between the affinity values varies inversely with the number of carbon atoms between the groups, except in the case of oxalic and succinic acids, the ratio of which shows a greater increase. In the dicarboxylic acid series the two carboxylic groups are mutually active, the one increasing the tendency of the other to be active or possess residual affinity, but the latter function varies inversely with the number of interposed methylene groups. The following formula for the dicarboxylic acids, in which these facts have been noted, is suggested:

$$CH_2 \Big\langle {}^{CH_2-CH_2-CO_2H}_{CH_2-CH_2-CO_2H} \Big)$$
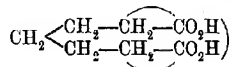
<div align="right">C. A. M.</div>

Method of Preparing Acetaldehyde. UNION CARBIDE Co. (U.S.-P., 1247270, 1917; from *J. Soc. Chem. Ind.*, 1918, **37**, 74A).—Acetylene is combined with the elements of water in an acid bath containing a mercury compound. The bath is maintained at such a temperature that the acetaldehyde distils continuously, and the mixture of acetaldehyde and acetylene is conducted into a series of baths similar to the first bath. W. P. S.

The Wagner-Saytzeff Reaction with Mesityl Oxide. C. J. ENKLAAR (*Chem. Weekblad*, 1918, **15**, 188—190).—The liquid obtained by the action of zinc, mesityl oxide, and allyl bromide, in presence of anhydrous ether, yields on distillation two fractions, in addition to unchanged products. The first fraction has b. p. 71°/20 mm., and consists of $\beta\delta$-dimethyl-$\Delta^{\beta\gamma}$-heptadien-δ-ol mixed with a smaller proportion of a ketone, $C_9H_{16}O$, probably a dimethyl-heptenone.

The second fraction has b. p. 140—142°/3 mm., and its constituents have not been identified. A. J. W.

Influence of different Compounds on the Destruction of Monosaccharides by Sodium Hydroxide and on the Inversion of Sucrose by Hydrochloric Acid. III. Constitutional Formulæ of the Hydroxybenzoic Acids and of Sulphanilic Acid. H. I. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 581—589. Compare A., 1917, i, 631; this vol., i, 101).—Salicylic acid behaves in alkaline solution as a monobasic acid in

CH
HC⟋＼C:O
HC＼⟋CH·CO₂H
CH
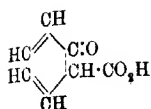
retarding the destruction of dextrose, whereas *m*- and *p*-hydroxybenzoic acids behave as dibasic acids. The author considers that these results support the constitutional formula (annexed) assigned to salicylic acid by Brunner (compare Holleman, "Die direkte Einführung von Substituenten in den Benzolkern," Leipzig, 1910).

Sulphanilic and hippuric acids behave as monobasic acids in alkaline solutions, and are neutral in their influence on the inversion of sucrose by hydrochloric acid. On these grounds the author assigns the constitution I to sulphanilic acid in alkaline solution and constitution II in acid solution.

NH_2 NH_3

$SO_2·OH$ SO_2 O

(I.)   (II.)
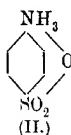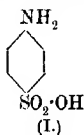
[See also *Ind.*, 189A.*]   W. G.

Lactose. II. A. SMITS and J. GILLIS (*Proc. K. Akad. Wetensch Amsterdam*, 1918, **20**, 573—580. Compare this vol., i, 101).— From a study of the results previously given (*loc. cit.*), coupled with those obtained by Hudson (compare A., 1909, ii, 131; 1910, i, 220), the authors consider that mutarotation is not due to a slow dehydration process in the sugar series, as was assumed by Hudson, but to the slow establishment of an internal equilibrium between two stereo-isomeric forms. Further, that for the unsubstituted aldoses, such as dextrose, galactose, lactose, etc., the presence of water of hydration does not change anything in the structure of the asymmetric terminal carbon atom. The pseudo-ternary $T - x$ figure of the system water–α-lactose–β-lactose is given, and the surface of equilibrium lying in it is shown.   W. G.

The Reduction of the Group ·CH_2I attached to Nitrogen. AMAND VALEUR and EMILE LUCE (*Compt. rend.*, 1918, **166**, 392—394. Compare this vol., i, 102).—Dimethyliodomethyl-δ-iodo-amylammonium iodide, $CHMeI·CH_2·CH_2·CH_2·NMe_2I·CH_2I$, when reduced by zinc in alcohol or in dilute acetic acid, gave trimethyl-amylammonium iodide, $CH_2Me·CH_2·CH_2·CH_2·NMe_3I$, together with a small amount of an unsaturated methiodide. Methylene-des-dimethylpiperidine iodide when similarly reduced gave des-di-methylpiperidine methiodide [trimethyl-Δ^δ-pentenylammonium iodide], m. p. 227—229°, giving an aurichloride, m. p. 107°. Di-methyliodomethyl-$\Delta\gamma$-pentenylammonium iodide,

$$CHMe:CH·CH_2·CH_2·NMe_2I·CH_2I,$$
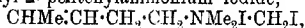
when reduced gave a mixture of two isomeric unsaturated *meth-iodides*, $C_8H_{18}NI$, giving two *aurichlorides*, having m. p.'s 116° (decomp.) and 89—91° respectively. Trimethyliodomethylammon-

* In cross references to abstracts, *Ind.* will be used in place of *J. Soc. Chem. Ind.*, 1918, **37**.

ium iodide when reduced by zinc and acetic acid yielded tetra-methylammonium iodide.
<div style="text-align: right">W. G.</div>

Isethionic Acid Derivatives of some Aliphatic Amino-acids. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1917, **101**, 1—14. Compare A., 1916, i, 815).

—A mixture of equimolecular quantities of the amino-acid and isethionic acid is dissolved in water, heated on the water-bath, and finally at 140—143° for three and a-half to four hours. The cooled mass is dissolved in water, and the product of the reaction precipitated by alcohol. It is then recrystallised from dilute alcohol with the aid of animal charcoal. *Isethionyl-glycine*, $CO_2H \cdot CH_2 \cdot NH \cdot SO_2 \cdot C_2H_4 \cdot OH$, does not melt below 260°; it gives a crystalline *copper* salt. *Isethionylalanine*, $C_5H_{11}O_5NS$, has m. p. 242° (decomp.), and *isethionylleucine*, $C_8H_{17}O_5NS$, m. p. 260° (decomp.). The three compounds have several properties in common; the aqueous solution is acid to litmus, but neutral to Congo-red, unless the solution is very concentrated. Phosphotungstic acid does not produce a precipitate, but only a turbidity, which disappears on warming and reappears on cooling. They reduce ammoniacal silver nitrate and when heated give off sulphur dioxide and a gas, of which the odour resembles that of mercaptan.

A similar compound appears to be formed between isethionic acid and aspartic acid, but it could not be isolated in a crystalline condition.
<div style="text-align: right">H. W. B.</div>

Action of Formaldehyde on Glycine and its Metallic Salts. HUGO KRAUSE (*Ber.*, 1918, **51**, 136—150).

—The use of formaldehyde in the titration of glycine is now a matter of common knowledge, but no definite work has yet appeared on the nature of the reaction between these compounds, or on the behaviour of the metallic salts of glycine. It is now shown that the salts react like the free amino-acid, and that the products, which may be isolated, in all cases correspond with a condensation product of the formula $C_7H_{14}O_5N_2$. Allowing $C_4H_8O_4N_2$ for two glycine residues, it follows that this product can only be written as

$$OH \cdot CH(CH_2 \cdot NH \cdot CH_2 \cdot CO_2H)_2.$$
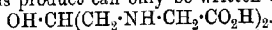
From a measurement of the amount of formaldehyde which takes part in the reaction, the very puzzling discovery is made that only one molecule of the aldehyde is required for one of the acid. This is explained by the fact that the methyl alcohol present in the formalin used also enters into the process. If pure formaldehyde solution is used, very little of the compound is formed, relatively much more formaldehyde disappears, and a considerable amount of formic acid is produced. It can be proved, moreover, by a rough quantitative method, that methyl alcohol disappears. The normal reaction is therefore expressed in the equation $2NH_2 \cdot CH_2 \cdot CO_2H + 2CH_2O + CH_3 \cdot OH = C_7H_{14}O_5N_2 + 2H_2O$, whilst the pure aldehyde reacts according to the equation $2NH_2 \cdot CH_2 \cdot CO_2H + 4CH_2O = C_7H_{14}O_5N_2 + H \cdot CO_2H + H_2O$.

The existence of the $-CH \cdot OH$ group in the molecule is proved by the facts that methyl and ethyl alcohols are formed on heating

the product, that the compound yields an acetate, and that acetone is formed, in traces, by oxidation with chromic acid.

A full account of the isolation of the products is given, and also of the application of the barium salt to the settlement of the above questions. Free β-*hydroxytrimethylenediglycine* is a deliquescent, white powder, which decomposes at above 75°, restores the colour of Schiff's reagent, and decomposes alkali carbonates with vigorous effervescence, and its *acetate* is also white. The *sodium* salt, $1H_2O$, and *calcium* salt, $2H_2O$, are deliquescent powders with alkaline reactions; the *barium* salt, $3H_2O$, crystallises in flat rods or leaflets, is not hygroscopic, and is only soluble in 22 parts of water at 18°; the *magnesium* salt, $3H_2O$, and an acid *salt*,

$$C_7H_{12}O_5N_2Mg,0\cdot25C_7H_{14}O_5N_2,2\cdot5H_2O,$$
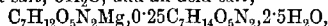
are somewhat hygroscopic; copper glycine gives a fairly insoluble deep blue *salt* of the formula $C_7H_{12}O_5N_2Cu,3H\cdot CHO$; with silver glycine, a white precipitate, probably of the normal salt, is formed momentarily, but this soon changes into a yellow *salt*, according to the equation, $C_7H_{12}O_5N_2Ag_2 + 2H_2O = 2OH\cdot CH_2\cdot NH\cdot CH_2\cdot CO_2Ag + CH_3\cdot OH$. 　　　　　　　　　　　　　　J. C. W.

Action of Ethyl Oxalate on Ethyl β-Aminocrotonate. WILHELM WISLICENUS and KARL SCHÖLLKOPF (*J. pr. Chem.*, 1917, [ii], **96**, 174—179).—The interaction of ethyl oxalate and ethyl β-aminocrotonate in the presence of alcoholic-ethereal potassium ethoxide follows the course stated by Benary, Reiter, and Svenderop (A., 1917, i, 252), the product being the yellow potassium derivative, $CO_2Et\cdot C(OK)\dot{:}N\cdot CMe\dot{:}CH\cdot CO_2Et$, of ethyl N-ethoxalylaminocrotonate, from which the free ester is liberated on acidifying. In the presence of water, the potassium derivative readily undergoes partial hydrolysis with formation of ethyl β-oxalylaminocrotonate, prisms, which after dehydration have m. p. 106—108°. If ethyl aminocrotonate is allowed to react with a bimolecular proportion of ethyl oxalate and of·potassium, a deep yellow dipotassium compound, $C_{12}H_{11}O_7NK_2$, is obtained, probably a cyclic derivative of ethyl N-C-diethoxalyl-β-aminocrotonate; on treatment with dilute mineral acid, the aqueous solution of this dipotassium compound deposits yellow needles of a *compound*, $C_{12}H_{12}O_7NK$, containing only one atom of potassium. 　　　　　　　　　　　　D. F. T.

The Nitrogenous Pigments of Molasses. H. FRIEDRICH (*Zeitsch. Zuckerind. Böhm.*, 1917, **41**, 769—771). VL. STANĚK (*ibid.*, 771—773).—Polemical. Friedrich's reply to Staněk's criticism (A., 1917, i, 545), and a rejoinder. 　　　　　J. C. W.

The Pseudo-system Methyl Thiocyanate, Methylthiocarbimide and Trimethyl Trithiocyanate. J. GILLIS (*Chem. Weekblad*, 1917, **15**, 48—78).—An investigation of the curves of solidification and ebullition of mixtures of methyl thiocyanate and methylthiocarbimide. 　　　　　　　　　　　A. J. W.

Organo-Cadmium Compounds. I. Simple Cadmium Alkyls. ERICH KRAUSE (*Ber.*, 1917, **50**, 1813—1822).—Cadmium dialkyls can be readily obtained by adding finely powdered, dry

cadmium bromide to ethereal solutions of the magnesium alkyl bromides and distilling the product in a high vacuum. The pure compounds are colourless, highly refractive oils with very unpleasant odours and irritating action on the mucous membrane. The lower members are remarkably volatile, especially in ether vapour, and it is also interesting that the boiling points range higher than those of the corresponding mercury dialkyls. The oils are permanent if stored in tubes filled with pure nitrogen in the dark, but with traces of air and moisture they soon become steely-blue, especially in the light. Cadmium dimethyl merely gets coated with a white crust of the methoxide on exposure to the air, but the others are vigorously oxidised, and even inflame if allowed to fall in drops. The oils sink in water, and then if shaken begin to decompose with a crackling noise, which proceeds for hours. They are mostly stable, in an indifferent atmosphere, up to about 180°, when they decompose so vigorously that part of the liberated metal melts to brilliant drops and another part is deposited as a mirror.

The atomic refraction and dispersion of cadmium in these alkyls rise steadily with the molecular weights, but, taking averages, they are remarkably high compared with the constants for mercury and zinc.

Cadmium dimethyl has m. p. $-4.5°$, b. p. $105.5°/758$ mm., $D_4^{17.9}$ 1.9846, n_{H_a} 1.57766, n_D 1.58488, n_{H_β} 1.60381, n_{H_γ} 1.62053, at $17.9°$. *Cadmium diethyl* has m. p. $-21°$, b. p. $64°/19.5$ mm., $D_4^{18.1}$ 1.6564, n_{H_a} 1.56512, n_D 1.56798, n_{H_β} 1.58447, n_{H_γ} 1.59887, at $18.1°$. *Cadmium di-n-propyl* has m. p. $-83°$, b. p. $84°/21.5$ mm., $D_4^{17.6}$ 1.4201, n_{H_a} 1.52412, n_D 1.52906, n_{H_β} 1.54267, n_{H_γ} 1.55452, at $17.6°$. *Cadmium di-n-butyl* has m. p. $-48°$, b. p. $103.5°/12.5$ mm., $D_4^{19.5}$ 1.3056, n_{H_a} 1.51100, n_D 1.51546, n_{H_β} 1.52762, n_{H_γ} 1.53793, at $19.5°$. *Cadmium diisobutyl* has m. p. $-37°$, b. p. $90.5°/20$ mm., D_4^{18} 1.2693, n_{H_a} 1.49528, n_D 1.49966, n_{H_β} 1.51160, n_{H_γ} 1.52173, at $18°$. *Cadmium diisoamyl* has m. p. $-115°$, b. p. $121.5°/15$ mm., D_4^{19} 1.2210, n_{H_a} 1.49967, n_D 1.50389, n_{H_β} 1.51470, n_{H_γ} 1.52412, at $19°$. All densities are reduced to vacuum standard.   J. C. W.

Some mixed Tin Tetra-alkyls and Tin Trialkyl Haloids. GERHARD GRÜTTNER and ERICH KRAUSE (*Ber.*, 1917, 50, 1802—1807).—The physical constants of some twenty known organo-tin compounds are tabulated, and an account is given of about twenty new compounds of the same nature. The material is being gathered for an investigation on the atomic refraction of tin and for studies on compounds containing tin chains (compare following abstract).

Mixed tin tetra-alkyls are prepared by heating tin trialkyl bromides with three times the theoretical quantity of magnesium alkyl haloids, first in ether and then at 100°, and they are converted into the tin trialkyl bromides by the action of bromine at $-40°$ to $-30°$, the rule being that the lightest alkyl group is displaced (compare lead; A., 1917, i, 256). The chlorides are made from the bromides by shaking their ethereal solutions with 33%

sodium hydroxide (or silver hydroxide in the case of the methyl compounds), and then adding hydrochloric acid to the ethereal extract of the tin trialkyl hydroxide.

Tin triethylisobutyl has b. p. 96·5°/17 mm., $D_4^{20\cdot3}$ 1·1390, n_{H_a} 1·46977, n_D 1·47304, n_{H_β} 1·48132, n_{H_γ} 1·48826, at 20·3°. *Tin dimethyldiiso-butyl* has b. p. 85°/16·5 mm., $D_4^{20\cdot1}$ 1·1179, n_{H_a} 1·46037, n_D 1·46354, n_{H_β} 1·47165, n_{H_γ} 1·47851, at 20·1°. *Tin triethylisoamyl* has b. p. 111°/18·5 mm., $D_4^{20\cdot1}$ 1·1203, n_{H_a} 1·46917, n_D 1·47243, n_{H_β} 1·48050, n_{H_γ} 1·48739, at 20·1°. *Tin ethyltri-n-propyl* has b. p. 117·5/23·5 mm., $D_4^{21\cdot3}$ 1·1225, n_{H_a} 1·47053, n_D 1·47374, n_{H_β} 1·48197, n_{H_γ} 1·48890, at 21·8°. *Tin diethyldiisobutyl* has b. p. 108·2°/13 mm., $D_4^{20\cdot4}$ 1·1030, n_{H_a} 1·47036, n_D 1·47361, n_{H_β} 1·48167, n_{H_γ} 1·48846, at 20·4°. *Tin tri-n-propylisobutyl* has b. p. 128°/18 mm., $D_4^{24\cdot1}$ 1·0841, n_{H_a} 1·46929, n_D 1·47245, n_{H_β} 1·48042, n_{H_γ} 1·48711, at 24·1°. *Tin diethyldiisoamyl* has b. p. 131°/13·5 mm., D_4^{19} 1·0725, n_{H_a} 1·46957, n_D 1·47268, n_{H_β} 1·48040, n_{H_γ} 1·48694, at 19°. *Tin ethyltriisobutyl* has b. p. 125°/16 mm., D_4^{21} 1·0779, n_{H_a} 1·47053, n_D 1·47371, n_{H_β} 1·48167, n_{H_γ} 1·48830, at 21°. *Tin ethyl-n-propyldiisoamyl* has b. p. 141—142°/17 mm., $D_4^{21\cdot9}$ 1·0654, n_{H_a} 1·46902, n_D 1·47214, n_{H_β} 1·47996, n_{H_γ} 1·48652, at 21·9°. *Tin tetraisobutyl* has m. p. -13°, b. p. 143°/16·5 mm., D_4^{23} 1·0540, n_{H_a} 1·47112, n_D 1·47423, n_{H_β} 1·48206, n_{H_γ} 1·48863, at 23°. *Tin triisobutylisoamyl* has b. p. 152·9°/16·5 mm., $D_4^{26\cdot8}$ 1·0356, n_{H_a} 1·46851, n_D 1·47174, n_{H_β} 1·47984, n_{H_γ} 1·48575, at 26·8°.

Tin diethyl-n-propyl chloride has b. p. 108°/17 mm., $D_4^{15\cdot7}$ 1·3848, n_{H_a} 1·50207, n_D 1·50580, n_{H_β} 1·51524, n_{H_γ} 1·52322, at 15·7°. *Tin diethylisoamyl chloride* has b. p. 125·5—126·5°/13 mm., $D_4^{19\cdot9}$ 1·2994, n_{H_a} 1·49443, n_D 1·49805, n_{H_β} 1·50687, n_{H_γ} 1·51443, at 19·9°. *Tin diethyl-n-propyl bromide* has b. p. 112·2°/16 mm., D_4^{21} 1·5910, n_{H_a} 1·51759, n_D 1·52177, n_{H_β} 1·53232, n_{H_γ} 1·54129, at 21°. *Tin diethylisobutyl bromide* has b. p. 122°/17 mm., D_4^{20} 1·5108, n_{H_a} 1·51194, n_D 1·51586, n_{H_β} 1·52609, n_{H_γ} 1·53464, at 20°. *Tin diethylisoamyl bromide* has b. p. 137·5°/17 mm., D_4^{17} 1·4881, n_{H_a} 1·51251, n_D 1·51651, n_{H_β} 1·52653, n_{H_γ} 1·53503, at 17°. *Tin ethyldiisobutyl bromide* has b. p. 130·6°/13 mm., $D_4^{19\cdot5}$ 1·4085, n_{H_a} 1·50452, n_D 1·50837, n_{H_β} 1·51799, n_{H_γ} 1·52607, at 19·5°. *Tin ethyldiisoamyl bromide* has b. p. 154—155°/16 mm., D_4^{20} 1·3650, n_{H_a} 1·50263, n_D 1·50631, n_{H_β} 1·51562, n_{H_γ} 1·52347, at 20°.

All densities are reduced to vacuum standard, and optical constants at higher temperatures are also recorded in one or two instances.

J. C. W

Hexa-alkyldistannanes. Atomic Linking of Tin. GERHARD GRÜTTNER (*Ber.*, 1917, **50**, 1808—1813).—Hexa-alkyldistannanes, $R_3Sn \cdot SnR_3$, are prepared by heating tin trialkyl bromides, diluted with an equal volume of ether, with sodium powder at 120°. They are colourless, highly refractive and dispersive liquids with very unpleasant, penetrating odours. They are stable towards heat and are only slowly oxidised on exposure to the air.

Hexaethyldistannane has b. p. 161—162°, $D_4^{17\cdot8}$ 1·3795, n_{H_a} 1·53224, n_D 1·53738, n_{H_β} 1·55065, n_{H_γ} 1·56210, at 17·8°. *Hexa-n-propyldistannane* has b. p. 143·6°/15 mm., $D_4^{19\cdot5}$ 1·2436, n_{H_a} 1·52122,

n_D 1·52583, $n_{H\beta}$ 1·53773, $n_{H\gamma}$ 1·54806, at 19·5°. *Hexaisobutyl-distannane* has b. p. 179°/3·5 mm., m. p. 43·8°, D_4^{20} 1·1330, $n_{H\alpha}$ 1·49706, n_D 1·50128, $n_{H\beta}$ 1·51191, $n_{H\gamma}$ 1·52120, at 59°. s.-*Tetra-ethyldi-n-propyldistannane*, $Sn_2Et_4Pr''_2$, has b. p. ·165·8°/15 mm., D_4^{20} 1·3313, $n_{H\alpha}$ 1·53042, n_D 1·53541, $n_{H\beta}$ 1·54822, $n_{H\gamma}$ 1·55945, at 15·3°. s.-*Tetraethyldiisobutyldistannane* has b. p. 179°/15·5 mm., $D_4^{19\cdot5}$ 1·2919, $n_{H\alpha}$ 1·52108, n_D 1·52571, $n_{H\beta}$ 1·53772, $n_{H\gamma}$ 1·54815, at 19·8°.
Densities are reduced to vacuum standard.   J. C. W.

Side-chain Chlorine Derivatives of Toluene (Benzyl and Benzylidene Chlorides and Benzotrichloride). H. D. GIBBS and G. A. GEIGER (U.S.-P., 1246739, 1917; from *J. Soc. Chem. Ind.*, 1918, **37**, 52A).

—Gaseous toluene and chlorine are introduced into a suitable reaction chamber in which they are subjected to the action of ultra-violet rays. One mol. of toluene with one, two, or three mols. of chlorine produces benzyl chloride, benzylidene chloride, and benzotrichloride, respectively.   W. P. S.

Bromination of p-Nitrotoluene. J. F. BREWSTER (*J. Amer. Chem. Soc.*, 1918, **40**, 406—407).

—In view of the usefulness of p-nitrobenzyl bromide in the characterisation of acids and phenols (see Reid, A., 1917, i, 333), it is of interest to know that satisfactory yields of the reagent can be obtained by gradually adding bromine dissolved in carbon tetrachloride to a boiling solution of p-nitrotoluene, containing a trace of iodine, and exposed to sunlight. [See also *Ind.*, April.]   J. C. W.

Sulphonation of Aromatic Hydrocarbons or their Derivatives. H. BULL (U.S.-P., 1247499, 1917; from *J. Soc. Chem. Ind.*, 1918, **37**, 52A).

—The sulphonation is carried out in the presence of an organic solvent of lower specific gravity than sulphuric acid in which the hydrocarbon and sulphonated substance are soluble. The solution of the sulphonated product is removed, and if this is done continuously, the process may be made continuous. The solvent may consist of an excess of the aromatic hydrocarbon.   W. P. S.

Tolane Chlorides from Calcium Carbide, Chlorine, and Benzene. CLINTON DAVIDSON (*J. Amer. Chem. Soc.*, 1918, **40**, 397—400).

—If powdered calcium carbide, free from iron, is added to cold benzene saturated with chlorine a reaction slowly sets in, the mixture becomes warm, and hydrogen chloride is evolved. After a time, the action subsides, even while much chlorine still remains. If the solution is then chilled, it deposits a mixture of the stable and labile forms of tolane dichloride, but if it is heated for several days until the b. p. rises to 100°, it will then give much tolane tetrachloride. Toluene reacts somewhat more readily, and apparently in the same way.

The mechanism of the process is indicated as follows:
$$CaC_2 + Cl_2 \longrightarrow CCl{:}CCl;$$
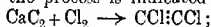
this $+ 2C_6H_6 \longrightarrow CPh\!:\!CPh$, and this $+ Cl_2 \longrightarrow CPhCl\!:\!CPhCl$ and $CPhCl_2\cdot CPhCl_2$. [See also *Ind.*, April.] J. C. W.

Coloured Condensation Products of Fluorene and Aldehydes.
Luis Guglialmelli and Angeles Delmon (*Anal. Soc. Quim. Argentina*, 1917, **5**, 124—130. Compare following abstract). —An account of colorations obtained by the action of fluorene in chloroform solution on aliphatic and cyclic aldehydes.
A. J. W.

Chromatic Reactions of Fluorene and Carbohydrates.
Luis Guglialmelli and Angeles Delmon (*Anal. Soc. Quim. Argentina*, 1917, **5**, 169—176. Compare preceding abstract).— Solutions of fluorene in chloroform and in alcohol give characteristic colour reactions with monoses, polyoses, polyhydric alcohols, and glucosides. A. J. W.

Addition of Ethyl Sodioacetoacetate to the Aromatic Mustard Oils [Thiocarbimides].
David E. Worrall (*J. Amer. Chem. Soc.*, 1918, **40**, 415—423).—Ethyl sodioacetoacetate reacts readily with phenyl-, the three tolyl-, *p*-bromophenyl-, and β-naphthyl-thiocarbimides according to the equation

$$Na\cdot CHAc\cdot CO_2Et + R\cdot N\!:\!C\!:\!S = CH_3\cdot CO\cdot CH(CO_2Et)\cdot C(SNa)\!:\!NR.$$
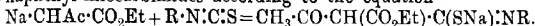
The products change into thioanilides, $NHR\cdot CS\cdot CHAc\cdot CO_2Et$, on acidifying with hydrochloric acid. In the case of the phenyl, para-substituted phenyl, and naphthyl compounds, these compounds suffer "acid hydrolysis" even with dilute alkali hydroxides, giving the fragments $NHR\cdot CS\cdot CH_2\cdot CO_2H$, AcOH, and EtOH, but the *o-* and *m*-tolyl compounds undergo "ketonic hydrolysis," yielding alcohol, carbon dioxide, and the substances $CH_2Ac\cdot CS\cdot NH\cdot C_6H_4Me$. Ethyl and benzyl derivatives of ethyl sodioacetoacetate react with phenylthiocarbimide less readily, and the products are more stable towards alkalis.

Ethyl sodioacetoacetate, obviously prepared in a non-hydroxylic solvent (ether), and phenylthiocarbimide yield *ethyl acetylthion-malonanilate*, $NHPh\cdot CS\cdot CHAc\cdot CO_2Et$, which crystallises in pale yellow, prismatic needles, m. p. 82—83°, yields hydrogen sulphide, ethyl acetate, and aniline hydrochloride when boiled with concentrated hydrochloric acid, and silver sulphide and acetaldehyde with warm silver nitrate, and changes into malonthionanilic acid, $NHPh\cdot CS\cdot CH_2\cdot CO_2H$ (Ruhemann, T., 1908, **93**, 624), on warming with sodium hydroxide.

o-Tolylthiocarbimide yields such an unstable primary product that it cannot be isolated. Ketonic hydrolysis takes place so readily that the product is *acetothionaceto-o-toluidide*,
$$COMe\cdot CH_2\cdot CS\cdot NH\cdot C_6H_4Me,$$
which crystallises in nearly colourless needles, m. p. 73—75°, and is hydrolysed by concentrated hydrochloric acid to acetic acid and Wallach's thionaceto-o-toluidide, $CH_3\cdot CS\cdot NH\cdot C_6H_4Me$ (the m. p. is
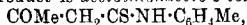
*k**

now given as 91—92° instead of 67—68°). *Acetothionaceto-m-toluidide* has m. p. 83—84°. *p*-Tolylthiocarbimide gives *ethyl acetylthionmalon-p-toluidate*, glistening, diamond-shaped tablets, m. p. 81° (the primary *sodium* derivative has m. p. 61—62°), and this yields *thionmalon-p-toluidic acid* on hydrolysis, in long, flat needles which melt at 97°, and change thereby into thionaceto-*p*-toluidide, m. p. 129·5—130·5° (Wallach).

Ethyl acetylthionmalon-p-bromoanilate has m. p. 81—83°; *thionmalon-p-bromoanilic acid* forms cream-coloured, flat needles and plates, and changes at 150° into *p-bromothionacetanilide*, which crystallises in narrow, hexagonal plates, m. p. 153°.

Ethyl acetylthionmalon-β-naphthylamate,

$$C_{10}H_7 \cdot CS \cdot CHAc \cdot CO_2Et$$

(not purified), yields *thionmalon-β-naphthylamic acid*, in pale yellow plates, m. p. 87—89° (decomp.).

Ethyl sodio-α-ethylacetoacetate gives *ethyl α-acetyl-α-ethyl-thionmalonanilate* as an oil, which is much more stable towards acids and alkalis than the above analogues. Ethyl sodio-α-benzyl-acetoacetate reacts very sluggishly with phenylthiocarbimide, and the only product described is a *polymeride* of, apparently, β-phenyl-thionpropionanilide, $CH_2Ph \cdot CH_2 \cdot CS \cdot NHPh$, having m. p. 222—223° (decomp.).   J. C. W.

Unsaturated Groups in Chemical and Pharmacological Connexions. I.

J. von Braun and Z. Köhler (*Ber.*, 1918, 51, 79—96).—That the unsaturated radicle, allyl, differs in many respects from aliphatic radicles is well known. Chemically, the most striking differences are to be found in its weaker attachments to nitrogen (compare Collie and Schryver, T., 1890, **57**, 767; von Braun, A., 1900, i, 641; Komatsu, A., 1913, i, 39), halogens (Clarke, T., 1910, **97**, 416; von Braun, A., 1912, i, 433), and oxygen (Claisen and Eisleb, A., 1913, i, 1175). Pharmacologically, it is a striking fact that by the replacement of an *N*-methyl group by allyl in choline or codeine, bases are obtained which are antagonistic to the parent bases (A., 1917, i, 254; 1916, i, 665).

The question naturally arises, are these effects peculiar to allyl or are they reproduced by other unsaturated radicles, and, if so, is the position of the ethylene linking of moment? The problem has therefore been attacked, and so far the chemical influences of the cinnamyl, $-CH_2 \cdot CH{:}CHPh$, the 2-furfuryl, $-CH_2 \cdot C{<}^{O-CH}_{CH \cdot CH}$, and Δ^{γ}-pentenyl, $-CH_2 \cdot CH_2 \cdot CH_2 \cdot CH{:}CH_2$, groups have been examined. It is found that the last resembles saturated radicles in its attachments, whilst the first two resemble allyl. An ethylene linking between the β- and γ-carbon atoms is therefore one factor of importance.

I. THE CINNAMYL RADICLE.—Cinnamyl bromide is conveniently prepared by heating cinnamyl alcohol with three times its weight of hydrobromic acid (D 1·48). The halogen is so loosely combined that it is quickly removed by warm water alone. The bromide

combines most readily with tertiary bases; for its behaviour with pyridine, see Clarke (*loc. cit.*); with trimethylamine, it forms *cinnamyltrimethylammonium bromide*, in silvery leaflets, m. p. 165°. It reacts vigorously with magnesium, the bromine being removed and $\alpha\zeta$-diphenyl-$\Delta^{\alpha\epsilon}$-hexadiene formed. With magnesium ethyl iodide, it yields this diphenylhexadiene and also *α-phenyl-Δ^{α}-pentene*, b. p. 202—205°, D_4^{22} 0·8782, n_D^{20} 1·51575. It condenses with dimethylamine to form *cinnamyldimethylamine*,

$$NMe_2 \cdot CH_2 \cdot CH \colon CHPh,$$
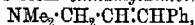
as a colourless liquid with strong basic odour, b. p. 100—101°/ 7 mm., which forms a *picrate*, m. p. 110°.

II. The 2-Furfuryl Radicle.—Furfuraldehyde is converted by Schwabbauer's method (A., 1902, i, 230) into 2-furfurylmethyl-amine, b. p. 59—60°/25 mm., which forms a *benzoyl* derivative, b. p. 180—185°/5 mm., and reacts with ethyl iodide to give *2-furfurylmethylethylamine*, $NMeEt \cdot CH_2 \cdot C \underset{CH \cdot CH}{\overset{O-CH}{<}}$. This is a colourless base which smells strongly like ammonia, has b. p. 69—70°/23 mm., forms a *picrate*, m. p. 91°, a *platinichloride*, m. p. 147°, and a *methiodide*, m. p. 101°, and reacts very vigorously with cyanogen bromide to give some *di-2-furfurylmethylethyl-ammonium bromide*, $(C_4H_3O \cdot CH_2)_2NMeEtBr$, m. p. 151°, a little methylethylcyanamide, $CN \cdot NMeEt$, but also, in 80% yield, the desired 2-furfuryl bromide. This is a very unstable oil, which severely attacks the mucous membrane, the skin, rubber, and cork, is quickly hydrolysed by warm water, and energetically combines with tertiary amines. *2-Furfuryltrimethylammonium platini-chloride*, m. p. 146—148° (decomp.), is mentioned in this connexion.

2-Furfurylmethylamine combines with ethylene oxide at 50° to form 2-*furfurylmethyl-β-hydroxyethylamine*,

$$C_4H_3O \cdot CH_2 \cdot NMe \cdot CH_2 \cdot CH_2 \cdot OH,$$
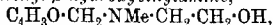
as a glycerol-like liquid, b. p. 105°/6 mm., which yields a *picrate*, m. p. 68—70°, a very soluble *aurichloride*, a *platinichloride*, decomp. 133°, and a *methiodide*, m. p. 77—80°.

III. The Δ^{δ}-Pentenyl Radicle.—The parent substance in this series is the dimethylpentenylamine, $CH_2 \colon CH \cdot [CH_2]_3 \cdot NMe_2$, which is obtained by the Hofmann degradation of piperidine. This reacts very vigorously with cyanogen bromide, about half of the base being converted into its methobromide, and the remainder into *methyl-Δ^{δ}-pentenylcyanamide*, $CH_2 \colon CH \cdot C_3H_6 \cdot NMe \cdot CN$. b. p. 96—98°/7 mm. This is hydrolysed by boiling with 25% sulphuric acid to *methyl-Δ^{δ}-pentenylamine*, a mobile liquid, b. p. 107—109°, which fumes in the air, and forms a *platinichloride*, m. p. 158°, a *picrate*, m. p. 150°, and a *benzoyl* derivative, b. p. 164—167°/ 7 mm. This amide, $CH_2 \colon CH \cdot C_7H_6 \cdot NMeBz$, gives the desired Δ^{δ}-pentenyl haloids on fusion with phosphorus pentahaloids, but the yields are very small. Another attempt to prepare the haloids was therefore made.

A solution of sodium amyloxide is cautiously warmed with

$\alpha\epsilon$-dichloropentane, when the di-ether, $C_5H_{10}(O \cdot C_5H_{11})_2$ (Hamouet, A., 1904, i, 705), and ϵ-*chlorodiamyl ether*, $C_5H_{11} \cdot O \cdot C_5H_{10}Cl$, are formed, the yield of the latter being 40%. This ether is a colourless, pleasant-smelling liquid, b. p. 100—105°/8 mm., which reacts with dimethylamine to form *dimethylamyloxyamylamine*, as a limpid liquid with penetrating odour, b. p. 99—103°/7 mm. [The amyloxy-residue in these compounds is derived from ordinary amyl alcohol; the prefix " g.-" is proposed, from Gärung = fermentation, to signify this.] The tertiary amine is hydrolysed by means of concentrated hydrochloric acid to *dimethyl-ϵ-chloroamylamine hydrochloride*, which is snow-white, and may be converted into the *aurichloride*, m. p. 64—65°. The free base is stable enough to be transformed into the *methiodide*, $C_5H_{10}Cl \cdot NMe_3I$, m. p. 134°, but this loses some chlorine as well as the iodine on treatment with silver oxide, so that on distilling the quaternary ammonium hydroxide only an impure specimen of the desired pentenyl chloride can be obtained.

The purest specimen of Δ^ϵ-*pentenyl bromide* so far obtained had b. p. 110°. It has a sweet odour, does not attack the eyes, is not readily attacked by water, does not combine easily with tertiary amines, but reacts fairly completely with magnesium, in all these respects differing from allyl bromide. Not sufficient magnesium Δ^ϵ-pentenyl bromide could be obtained in this way for any experiments, but the compound was prepared from $\alpha\delta\epsilon$-tribromopentane, as follows.

ϵ-Phenoxyamyl iodide is treated with trimethylamine, the quaternary iodide is converted into the hydroxide, and this is distilled, when a 40% yield of ϵ-*phenoxy-Δ^α-pentene* is obtained as a pleasant-smelling, limpid liquid, b. p. 109—111°/13 mm., D_4^0 0·9464, n_D^{20} 1·50. The *dibromide* of this, b. p. 190—205°/ 12 mm., is hydrolysed by prolonged boiling with fuming hydrobromic acid to $\alpha\delta\epsilon$-*tribromopentane*, which is a heavy oil, b. p. 128—132°/11 mm., with spicy odour. This behaves like other tribromides which contain two bromine atoms attached to neighbouring carbon atoms when treated with magnesium (A., 1911, i, 701, 938), the chief product being magnesium Δ^ϵ-pentenyl bromide, $CH_2 \colon CH \cdot C_3H_6 \cdot MgBr$. This is proved by the fact that Δ^ϵ-hexenoic acid, $CH_2 \colon CH \cdot C_3H_6 \cdot CO_2H$. is produced from it by the action of carbon dioxide (compare Fichter and Langguth, A., 1897, i, 590).

J. C. W.

Dicyclohexylamine.   Solid   Hydrate   and   Alcoholate.
GUSTAVE FOUQUE (*Compt. rend.*, 1918, **166**, 394—395).—Dicyclohexylamine, when poured on to water at below 23°, gave a crystalline *hydrate*, $NH(C_6H_{11})_2,H_2O$, m. p. 23°. The solubility of the amine in water, and of water in the amine, diminished as the temperature rose above 23°. An equimolecular mixture of dicyclohexylamine and ethyl alcohol at the ordinary temperature gave the *alcoholate*, $NH(C_6H_{11})_2,EtOH$, m. p. 28°, which dissociated in the air.   W. G.

Oxalyl Chloride as a Reagent in Organic Chemistry.
II. Preparation of Aromatic Anhydrides. Reaction with Alcohols.

Roger Adams, W. V. Wirth, and H. E. French (*J. Amer. Chem. Soc.*, 1918, **40**, 424—431. Compare A., 1916, i, 140; 1917, i, 4).—When slightly more than one molecular proportion of oxalyl chloride is added to a boiling solution of two parts of an aromatic acid in benzene, very good yields of the acid anhydride are obtained. The reaction apparently proceeds in two stages, thus: $2R \cdot CO_2H + C_2O_2Cl_2 = 2HCl + (R \cdot CO \cdot O)_2C_2O_2$, and this $= (R \cdot CO)_2O + CO + CO_2$, for *m*-nitro-, 2:4- and 3:5-dinitro-benzoic acids yield the intermediate mixed anhydrides (probably owing to the insolubility of these in benzene), which decompose in the indicated way on heating or on treatment with cold pyridine.

The advantages of the method are obvious. The following anhydrides have been prepared in this way: benzoic; the three toluic; *o-chlorobenzoic*, white, prismatic needles, m. p. 78—79°; *m-chlorobenzoic*, short, white needles, m. p. 95°; *p*-chlorobenzoic; *m-iodobenzoic*, plates, m. p. 134°; *o*-nitrobenzoic; *m-nitrobenzoic oxalic anhydride*, $(NO_2 \cdot C_6H_4 \cdot CO \cdot O)_2C_2O_2$, pale yellow, decomposing at 157° into *m-nitrobenzoic anhydride*, m. p. 163° [Autenrieth's anhydride, m. p. 47° (A., 1901, i, 186), was really Greene's *m*-nitrobenzoic acetic anhydride, $Ac \cdot O \cdot CO \cdot C_6H_4 \cdot NO_2$ (A., 1890, 53)]; 3:5-*dinitrobenzoic oxalic anhydride*, decomp. 175°, and 3:5-*dinitrobenzoic anhydride*, m. p. 109°; 2:4-*dinitrobenzoic oxalic anhydride*, m. p. 205—209° (decomp.), and 2:4-*dinitrobenzoic anhydride*, m. p. 160°.

Just as phenols react with oxalyl chloride in the presence of pyridine, at 0°, to form oxalates, so primary and secondary alcohols give these esters in 50% yield, on an average. Tertiary alcohols usually do not react at all. The following *oxalates* have been prepared by this method: *benzhydryl*, m. p. 142—143°; *phenyl-o-tolylcarbinyl*, $(CHPh \cdot C_6H_4Me)_2C_2O_4$, m. p. 86—87°; *benzoin oxalate*, $(COPh \cdot CHPh)_2C_2O_4$, m. p. 243—245°; *piperonoin oxalate*, $C_{34}H_{26}O_8$, m. p. 225—226°; bornyl; menthyl; *isopropyl*; and *diphenylmethylcarbinyl oxalate*, $(CMePh_2)_2C_2O_4$, pyramids, decomp. 170—185° (yield very small). [See also *Ind.*, April.]
                                                              J. C. W.

Preparation of Solutions of Glycol Esters.

Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P., 298185, 1915; from *Chem. Zentr.*, 1917, ii, 145).—Ethylene glycol monobenzoate, m. p. 45°, can be dissolved in almost any proportion in solutions of the alkali salts of benzoic, toluic, salicylic, or cresotic acid; in place of the benzoyl derivative of ethylene glycol, the corresponding *m*- and *p*-toluoyl, *o*-chlorobenzoyl, or salicyl compound may be used.
                                                              D. F. T.

Preparation of Acyl Derivatives of Aromatic Amides.

Mendel Perelstein and Emil Bürgi (D.R.-P., 297875, 1915; from *Chem. Zentr.*, 1917, ii, 144—145).—By introducing the *iso*valeryl radicle into the amino-group of aromatic amides, compounds are

obtained possessing the soporific power of the amides, but much less poisonous. The method of preparation is by the direct interaction of the *isovaleryl* haloid with the acid amide, either in the molten condition or dissolved in an organic solvent in the presence of a dehydrating agent. By brominating the *isovaleryl*-substituted amide or by using an *α*-bromo*iso*valeryl haloid for the first reaction, it is possible to produce compounds of especial therapeutic value. The following substances were obtained: *cinnamoyl-α-bromoisovalerylamide*, colourless needles, m. p. 118° (*dibromide*, crystals, m. p. 145° with reddening); *benzoyl-α-bromoisovaleryl-amide*, colourless needles, m. p. 142—143°; *bis-α-bromoisovaleryl-salicylamide* [*α-bromoisovaleroxybenzoyl-α-bromoisovalerylamide*] needles, m. p. 119°; *benzoylisovalerylamide*, needles, m. p. 89°; *cinnamoylisovalerylamide*, needles, m. p. 103° (*dibromide*, m. p. 165°). D. F. T.

The Walden Inversion. VI. Influence of the Solvent on the Sign of the Product in the Conversion of Phenylbromo-acetic Acid into Phenylaminoacetic Acid. GEORGE SENTER and STANLEY HORWOOD TUCKER (T., 1918, **113**, 140—151; compare A., 1915, i, 535; 1916, i, 815; 1917, ii, 301).—It was found in the first experiments of this series that the sign of the amino-acid obtained by the action of ammonia on active phenylchloroacetic acid depends on the nature of the solvent employed, and it appeared to be of interest to examine this phenomenon in other cases.

Experiments on the displacement of bromine by the amino-group in the case of *l*-phenylbromoacetic acid have given the following results: (*a*) in aqueous solution, or in the higher alcohols (*n*-butyl, trimethylcarbinol, *n*-heptyl), the amino-acid obtained is opposite in sign, which agrees with the behaviour of phenylchloroacetic acid; (*b*) in the lower alcohols (methyl, ethyl, *n*- and *iso*-propyl) the product is also opposite in sign, whereas the amino-acid obtained from phenylchloroacetic acid in these solvents has the same sign as the parent halogeno-acid; (*c*) in acetonitrile or liquid ammonia, the product has the same sign, as in the earlier case; (*d*) considerable racemisation takes place in the lower alcohols, but not in the higher; (*e*) the presence of ammonium bromide has little racemising influence in aqueous solution, but considerable in liquid ammonia; (*f*) small quantities of iminodiphenyldiacetic acid, of high activity, opposite in sign to the original acid, are formed in all solvents.

The mechanism of the formation of the imino-acid is discussed. It is probable that it is formed by the direct action of ammonia on two molecules of the halogeno-acid, rather than by the interaction of the halogeno-acid with the amino-acid. J. C. W.

The Walden Inversion. VII. Influence of the Solvent on the Sign of the Product in the Conversion of *α*-Bromo-*β*-phenylpropionic Acid to *α*-Amino-*β*-phenylpropionic Acid (Phenylalanine). Iminodiphenyldipropionic Acid. GEORGE SENTER, HARRY DUGALD KEITH DREW, and GERALD HARGRAVE MARTIN (T., 1918, **113**, 151—163).—*α*-Bromo-*β*-phenylpropionic

acid has been examined in this series as the phenyl group is removed from the asymmetric carbon atom, and consequently different results might perhaps be anticipated. It is found that in all the solvents tried, water, alcohols, and even acetonitrile and liquid ammonia, the amino-acid has the opposite sign to the parent active acid, although very considerable racemisation occurs in the last two media. The most remarkable difference between this case and the earlier ones is, however, that ammonium bromide actually lessens racemisation when the reaction is carried out in liquid ammonia.

a-*Imino-ββ-diphenyldipropionic acid*, $NH[CH(CH_2Ph)\cdot CO_2H]_2$, is formed in small amounts in all the solvents, with the same sign as the bromo-acid.

The perplexing differences observed in the three cases (papers V., VI., and VII.) are perhaps best accounted for on the assumption that the action of ammonia on the halogeno-acids proceeds as two simultaneous reactions, the formation of both *d*- and *l*-amino-acids. Which of these reactions predominates depends on the nature of the acid, the nature of the solvent, and other factors.

[For experimental details, see the original.]   J. C. W.

Preparation of a Solid *iso***Valeric Acid Compound Soluble in Water.** HUGO VOSWINCKEL (D.R.-P., 294877, 1914 ; from *Chem. Zentr.*, 1917, ii, 144).—By warming a mixture of *iso*valeryl chloride and mandelic acid in benzene solution, *isovaleryl-mandelic* [a-*isovaleryloxyphenylacetic*] *acid*,

$$C_4H_9\cdot CO\cdot O\cdot CHPh\cdot CO_2H,$$
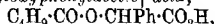
hard crystals, m. p. 71°, is obtained, the *calcium* salt of which is a granular solid soluble in water.   D. F. T.

Phthalic Acid Derivatives : Constitution and Colour. V. Some Derivatives of Tetrachloro- and Tetraiodo-phthalimides. DAVID S. PRATT and GRANVILLE A. PERKINS (*J. Amer. Chem. Soc.*, 1918, **40**, 198—214. Compare A., 1914, i, 415 ; 1915, i, 686, 692).—In the hope of obtaining a clearer insight into the relationship between the absorption bands shown by various members of the same family and a more exact knowledge of the origin of each band, investigation is being made of the absorption spectra of a large number of compounds related to phthalic acid, each differing only slightly from its neighbours. The present paper only deals with the preparation of phthalic acid derivatives in which halogen is substituted into the benzene ring, or in which the anhydride oxygen is replaced.

Tetrachlorophthalic anhydride, prepared by the action of chlorine on a hot solution of phthalic anhydride in fuming sulphuric acid in the presence of iodine, gives unstable, deeply coloured additive compounds with certain amines; with dimethylaniline and dimethyl-*p*-toluidine the *additive* compounds were isolated as red prisms, $C_8O_3Cl_4,NPhMe_2$. and almost purple crystals,

$$C_8O_3Cl_4,C_7H_7\cdot NMe_2,$$
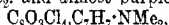
respectively, but the formation of similar compounds with diethylamine, methylaniline, and the two naphthylamines could only be

detected by the red colour of mixtures of the anhydride and the respective bases, dissolved in xylene if necessary; diphenylamine and aniline yielded yellow solutions, whilst no colour change was observed with pyridine and triethylamine; the presence of chlorine is not essential to this reaction because 3-nitrophthalic anhydride and other substituted phthalic anhydrides, including, indeed, even phthalic anhydride itself, are capable of similar behaviour, the effect being so general as to suggest that the formation of such additive compounds is an essential first stage in the condensation of phthalic anhydride and its nuclear substituted derivatives with aromatic amines. In these additive compounds it is believed that the attachment between the two molecules occurs by means of residual valency at the anhydride oxygen atom and the nitrogen atom of the amine; with a tertiary amine no further change is possible, but with a secondary amine rearrangement subsequently occurs with formation of the colourless salt, whilst with a primary amine, such as aniline, the formation of the aniline phthalanilate can be succeeded by loss of aniline and production of the anil. In accordance with this view, the yellow solution of tetrachlorophthalic anhydride and aniline in benzene gradually deposits *aniline tetrachlorophthalanilate*, $C_{20}H_{14}O_3N_2Cl_4$, a colourless, crystalline powder, m. p. 271—273° (corr.), which readily undergoes further condensation to tetrachlorophthalanil, m. p. 274—275° (corr.). When tetrachlorophthalic anhydride is heated with aniline, preferably in an inactive atmosphere, the reaction goes still further with production of *3-anilino-4 : 5 : 6-trichlorophthalanil*, $C_{20}H_{11}O_2N_2Cl_3$, orange blades, m. p. 179·5—180·5° (corr.), and a *dianilinodichlorophthalanil*, $C_{26}H_{17}O_2N_3Cl_2$, bright, scarlet blades, m. p. 182·5—183·5° (corr.). *Tetrachlorophthal-o-tolil*, $C_{15}H_7O_2NCl_4$, colourless, rhombic leaflets, m. p. 232—236·5° (corr.), also its meta-*isomeride*, m. p. 245·5—246·5° (corr.), and para-*isomeride*, were obtained by heating a solution of tetrachlorophthalic anhydride and the corresponding toluidine in acetic acid. Tetrachlorophthal-o-tolil exhibits dimorphism, separating from acetic acid or alcohol in colourless, hexagonal leaflets, which at 207° (corr.) soften and become yellow with formation of a coloured modification, m. p. 214—214·5° (corr.); this is stable only above 118°, and can also be obtained in long, hair-like crystals by seeding the warm solution of the ordinary form in acetic acid or alcohol with a little of the yellow form. In accordance with the probability that the yellow form below its transition point must possess more free energy than the colourless modification, it is found that the former yields coloured *additive* compounds with benzene (3 or $4C_{15}H_7O_2NCl_4, C_6H_6$, long, yellow, hair-like crystals), *m*-xylene ($4C_{15}H_7O_2NCl_4, C_6H_4Me_2$), nitrobenzene

$$(4C_{15}H_7O_2NCl_4, C_6H_5 \cdot NO_2,$$

yellow blades), and dimethylaniline ($5C_{15}H_7O_2NCl_4, NMe_2Ph$, scarlet needles), whereas the colourless variety shows no such tendency. The following anils were obtained by heating together the corresponding base and tetrachlorophthalic anhydride in acetic acid solution: *tetrachlorophthal-o-nitroanil*, $C_{14}H_4O_4N_2Cl_4$, colourless

leaflets, m. p. 272—273° (corr.); *tetrachlorophthal*-m-*nitroanil*, colourless blades, m. p. 300—301·5° (corr.); *tetrachlorophthal*-p-*nitroanil*, fine, colourless needles, m. p. 292—297° (corr.); *tetra-chlorophthal*-p-*hydroxyanil*, $C_{14}H_5O_3NCl_4$, bright yellow needles, m. p. 305—307° (corr.); *tetrachlorophthal*-p-*acetylaminoanil*, pale yellow nodules or colourless needles, m. p. near 339° (corr.).

For the preparation of tetrachlorophthalimide, m. p. 338—339° (corr.), Graebe's method (*Annalen*, 1887, **238**, 332) is less convenient than one employing formamide in place of ammonia, a warm solution of the tetrachlorophthalic anhydride in the former rapidly depositing the imide. In a similar manner tetra-iodophthalic anhydride reacts with formamide, giving *tetraiodophthalimide*, $C_8HO_2NI_4$, fine, yellow needles, m. p. 370—380° (decomp.), whilst condensation of the anhydride with the various aromatic amines in nitrobenzene solution gives *tetraiodophthalanil*, $C_{14}H_5O_2NI_4$, yellow blades, m. p. 314—315° (corr.); *tetraiodophthal*-o-*tolil*, $C_{15}H_7O_2NI_4$, minute, yellow crystals, m. p. 314—315° (corr.); *tetraiodophthal*-m-*tolil*, yellow blades, m. p. 325—326°; *tetraiodophthal*-p-*tolil*, yellow blades, m. p. 317—318° (corr.); *tetraiodophthal*-m-*nitroanil*, $C_{14}H_4O_4N_2I_4$, yellow, matted needles, m. p. 318—319° (corr.); *tetra-iodophthal*-p-*hydroxyanil*, $C_{14}H_5O_3NI_4$, fine, yellow needles, m. p. 330—336° (corr.), and *tetraiodophthal*-p-*acetylaminoanil*, minute, yellow blades, m. p. 339° (corr., decomp.). D. F. T.

Phthalic Acid Derivatives: Constitution and Colour. VI. Action of Amines on Dichlorophthalic Anhydrides. DAVID S. PRATT and GRANVILLE A. PERKINS (*J. Amer. Chem. Soc.*, 1918, **40**, 214—218. Compare preceding abstract).—3:4-Dichlorophthalic acid reacts with aniline in boiling acetic acid solution, yielding 3:4-*dichlorophthalanil*, $C_{14}H_7O_2NCl_2$, which usually crystallises in very pale yellow, silky needles, m. p. 174° (corr.), but on account of the readiness of transformation into a second modification, colourless prisms, m. p. 182—182·5° (corr.), the lower m. p. can be observed only by sudden immersion of a small quantity of the needles in a bath near 174°. When heated with an excess of aniline in an inert atmosphere, the dichlorophthalic acid undergoes further conversion into 3-*anilino*-4-*chlorophthalanil*, $C_{20}H_{13}O_2N_2Cl$, orange leaflets, m. p. 159·5—160°. In a similar manner, 3:6-dichlorophthalic acid is convertible into 3:6-dichlorophthalanil, m. p. 197—198° (corr.), and 3-*anilino*-6-*chlorophthalanil*, $C_{20}H_{13}O_2N_2Cl$, which exhibits dimorphism, the crystals commonly obtained from alcohol forming orange needles, which on rapid heating have m. p. 141° (corr.), whereas on slow heating or on being kept in contact with the substance becomes changed into a second form, small, orange prisms, m. p. 160—160·5°. 4:5-Dichlorophthalic anhydride reacts with aniline in boiling acetic acid, yielding 4:5-*dichlorophthalanil*, colourless, rhombic leaflets, m. p. 212·5—213° (corr.), but shows no tendency to the further replacement of chlorine by the anilino-group. D. F. T.

Phthalic Acid Derivatives: Constitution and Colour. VII. Di-iodo-, Tri-iodo-, and Dichloroiodo-phthalic Acids. DAVID S. PRATT and GRANVILLE A. PERKINS (*J. Amer. Chem. Soc.*, 1918, **40**, 219—236. Compare preceding abstracts).—In extension of the investigation in which chlorine in halogenated phthalanils was observed to be replaceable by the anilino-group, various iodo-phthalic acids were prepared for interaction with aniline.

When phthalic anhydride dissolved in fuming sulphuric acid is treated with iodine the composition of the product is dependent on the temperature; prolonged heating at 75° gives rise to nearly equal amounts of the 3:4- and 3:6-di-iodo-acids with much smaller quantities of 4:5-di-iodophthalic acid and 3:4:6-tri-iodophthalic anhydride, whereas the product obtained on rapid heating to 200° contains approximately the same amount of the 4:5-di-iodo-acid with a larger amount of the 3:4-di-iodo-acid and the tri-iodo-anhydride at the expense of the 3:6-di-iodo-acid. Traces of 4-iodo-phthalic acid and tetra-iodophthalic anhydride were also observed. A partial separation of the products is possible by esterification, only the 4:5-di-iodo-acid and part of the 3:4-di-iodo-acid forming normal esters with alcohol and hydrogen chloride. Separation was finally effected, however, by fractional precipitation from a solution of the disodium salts with acetic acid, causing deposition of the monosodium salts in the order 4:5-di-iodo-acid, tri-iodo-acid, and 3:4-di-iodo-acid, the salt of the 3:6-di-iodo-acid remaining in solution, aided by the knowledge that on recrystallisation from acetic acid the 3:4- and 4:5-di-iodo-acids separate unchanged, whereas the 3:6-di-iodo-acid and the tri-iodo-acid become converted into the corresponding anhydrides, which are very soluble in benzene. The structure of the various acids was determined by heating with sodium hydroxide solution and examination of the resulting hydroxy-acids. The dichlorophthalic anhydrides can be iodinated in a similar manner to the parent phthalic anhydride.

3:4-*Di-iodophthalic acid*, $C_8H_4O_4I_2$, colourless leaflets, m. p. 212—213° (corr.), when heated with acetic anhydride in benzene solution, yields the corresponding *anhydride*, $C_8H_2O_3I_2$, almost colourless prisms, m. p. 198—198·5° (corr.), is slowly hydrolysed by sodium hydroxide solution with formation of 3:4-dihydroxybenzoic acid, and reacts with aniline in boiling acetic acid, forming an *anil*, $C_{14}H_7O_3NI_2$, very pale yellow prisms, m. p. 270—271° (corr.).

3:6-*Di-iodophthalic acid* forms colourless leaflets which undergo gradual dehydration even below 100° with formation of the *anhydride*, colourless prisms, m. p. 234·5—235·5° (corr.). When heated with aqueous sodium hydroxide, 3-hydroxyphthalic acid is produced with much tarry matter, but no 3:6-dihydroxy-acid; however, by boiling a solution of the anhydride with aqueous pyridine and silver sulphate it is possible to obtain 6-*iodo*-3-*hydroxyphthalic anhydride* (*acetate*, $C_{10}H_5O_5I$, square crystals, m. p. 148·5—152·5°, corr.). which is hydrolysable with concentrated sodium hydroxide solution to 3:6-dihydroxyphthalic acid. 3-Hydroxyphthalic acid, $C_8H_6O_5$, colourless prisms, m. p. 161—163° (corr.; decomp.). readily passes into the anhydride, orange-yellow crystals, m. p. 198—199° (corr.;

Jacobsen, A., 1883, 1124, gives 145—148°), the *acetate* of which crystallises in colourless leaflets, m. p. 113·5—115·5° (corr.), and the *benzoate* in leaflets, m. p. 147·5—148° (corr.). 3:6-Di-iodophthal-anil, prepared similarly to its 3:4-isomeride, forms colourless, rect-angular plates, m. p. 233·5—234° (corr.).

4:5-*Di-iodophthalic acid*, colourless needles (probably with acetic acid of crystallisation) or leaflets, m. p. 221—222° (corr.; decomp.), on dehydration with acetic anhydride or by mere heating is con-verted into the *anhydride*, colourless prisms, m. p. 216·5—217° (corr.); hydrolysis of the acid with sodium hydroxide yields 4:5-di-hydroxyphthalic acid and perhaps a little 3:4:5-trihydroxyphthalic acid. 4:5-*Di-iodophthalanil*, prepared by heating the acid with acetic anhydride and aniline in acetic acid solution, exhibits dimorphism, separating from acetic acid or xylene in pale yellow needles, which on rapid heating have m. p. 231·5—233° (corr.), but on gradual heating undergo transformation into a modification, m. p. 241·5—243° (corr.), the latter being also obtained in the form of pale yellow, hexagonal leaflets from the molten anil on very slow cooling.

3:4:6-*Tri-iodophthalic anhydride*, $C_8HO_3I_3$, bright yellow, rhombic pyramids, m. p. 230—231° (corr.), yields an *anil*, $C_{14}H_6O_2NI_3$, light yellow, microscopic needles, m. p. 254·5—255·5° (corr.), and on hydrolysis with sodium hydroxide gives a mixture of 3:6-dihydroxyphthalic acid with other substances, probably including a little 3:5-dihydroxybenzoic acid.

3:4-*Dichloro*-5:6-*di-iodophthalic anhydride*, $C_8O_3Cl_2I_2$, yellow prisms, m. p. 229·5—230·5° (corr.), obtained by the interaction of 3:4-dichlorophthalic anhydride and iodine in heated fuming sul-phuric acid, yields an *anil*, $C_{14}H_5O_2NCl_2I_2$, pale yellow needles, m p. 242·5—243·5° (corr.). 3:6-*Dichloro*-4:5-*di-iodophthalic an-hydride*, yellow prisms, m. p. 258—258·5° (corr.), obtained in a similar manner, yields an *anil*, pale yellow needles, m. p. 232—232·5° (corr.). 4:5-*Dichloro*-3:6-*di-iodophthalic anhydride*, yellow blades, m. p. 232—233·5° (corr.), forms an *anil*, very pale yellow needles, m. p. 282·5—284° (corr.), and when heated with excess of aniline for twenty-four hours at 130° undergoes further conversion into 4:5-*dichloro*-3:6-*dianilinophthalanil*,

$$C_{26}H_{17}O_2N_3Cl_2,$$
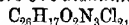
orange-red crystals, m. p. 181·5—185° (corr.), quite distinct from the isomeric product obtained by the action of aniline on tetra-chlorophthalanil (this vol., i, 168).   D. F. T.

Phthalic Acid Derivatives. Constitution and Colour. XII. Tetrachlorophthaloxime and some of its Derivatives. DAVID S. PRATT and CHARLOTTE H. MILLER (*J. Amer. Chem. Soc.*, 1918, **40**, 407—412. Compare preceding abstracts).—Unsubsti-tuted phthaloxime exists in two chromoisomeric forms (A., 1912, i. 190), but only one colour has been observed with the tetrachloro- and tetraiodo-phthaloximes and their ethers and esters. The ethers of tetrachlorophthaloxime, however, often exist in two modifications,

usually cotton-like masses and stable, stout prisms, which are inter-changeable, and this dimorphism has not been observed in the other series.

Tetrachlorophthaloxime (A., 1913, i, 100) forms a red *silver* salt, from which the following colourless ethers,

$$C_6Cl_4 \diagdown \begin{matrix} CO \longrightarrow \\ C(:N \cdot OR) \end{matrix} \diagup O,$$
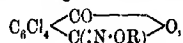
may be prepared: *methyl*, blades, m. p. 206°; *ethyl*, m. p. 160°; iso*propyl*, very thin, glistening plates or clusters of stout prisms, m. p. 146°; iso*amyl*, m. p. 244°; *allyl*, m. p. 186°; and *benzyl*, filaments only, m. p. 192°. The acetate (*ibid.*) and *benzoate*, pearly, diamond-shaped plates or stout prisms, m. p. 210°, are also obtained from the silver salt.

Tetrachlorophthalic anhydride phenylhydrazone,

$$C_6Cl_4 \diagdown \begin{matrix} CO \longrightarrow \\ C(:N \cdot NHPh) \end{matrix} \diagup O,$$
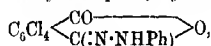
from the anhydride, phenylhydrazine, and glacial acetic acid, crystallises in yellow plates, which rapidly pass into orange needles, m. p. 287°. All m. p.'s are "corrected." [See also *Ind.*, April.]
                                                                J. C. W.

Phthalic Acid Derivatives. Constitution and Colour. XIII. Tetra-iodophthaloxime and some of its Derivatives. DAVID S. PRATT and THOMAS B. DOWNEY (*J. Amer. Chem. Soc.*, 1918, **40**, 412—415).—Tetra-iodophthalic anhydride (this vol., i, 177) has been converted into *tetra-iodophthaloxime,*

$$C_6I_4 \diagdown \begin{matrix} CO \longrightarrow \\ C(:N \cdot OH) \end{matrix} \diagup O,$$
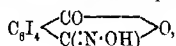
which exists in only one form, long, lemon-yellow needles of no definite m. p. From the red *silver* salt, the *methyl*, *ethyl*, n-*propyl*, iso*propyl*, n-*butyl*, iso*amyl*, n-*octyl*, *allyl*, and *benzyl* ethers, and the *acetate* and *benzoate*, have been obtained. These all crystallise in more or less pale yellow needles, and also decompose without melting. [See also *Ind.*, April.]   J. C. W.

The Structure of Truxillic Acids. A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 590—596).—From a consideration of their properties, their inter-conversion, and their preparation from cinnamic acids, the author has assigned spacial formulæ to the α-, β-, γ-, δ-, and ε-truxillic acids and to β-cocaic acid, on the assumption that these acids contain a tetramethylene ring.   W. G.

New Synthesis of Digallic Acid, and Migration of Acyl in the Partial Hydrolysis of Acylated Phenolcarboxylic Acids. EMIL FISCHER, MAX BERGMANN, and WERNER LIPSCHITZ (*Ber.*, 1918, **51**, 45—79).—Two syntheses have already been described which were expected to lead to *p*-digallic acid, but yielded

m-digallic acid instead (A., 1908, i, 893; 1911, i, 875; 1913, i, 479). A third method is now described. 3:5-Diacetylgallic acid is condensed with triacetylgalloyl chloride, giving penta-acetyl-*p*-digallic acid, and this is cautiously hydrolysed by cold, dilute ammonia solution. Again, the surprising discovery has been made that the product is *m*-digallic acid.

Similarly, if 3:5-diacetylgallic acid is benzoylated and the acetyl groups are removed by hydrolysis, the product is not para-, but *m*-benzoylgallic acid, and when 4-benzoyloxy-3-acetoxybenzoic acid is partly hydrolysed, the product is 3-benzoylprotocatechuic acid.

All these unexpected products are therefore due to the wandering of one acyl group into the position vacated on hydrolysis by another attached to a neighbouring carbon atom. Thus:
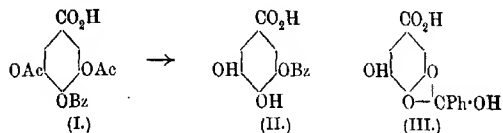
A transference of an acyl group has often been reported before, but only from carbon to oxygen or nitrogen and vice versa, or from nitrogen in a side-chain to nitrogen in the ring, numerous references to which are quoted, but this is the first record of such a migration from one phenolic group to another. The intermediate compound, (III), might perhaps be formed.

DERIVATIVES OF GALLIC ACID.—Triacetylgallic acid is conveniently obtained by adding granulated zinc chloride (50 grams) to a mixture of gallic acid (500) and acetic anhydride (2500). If too much zinc chloride is used, considerable quantities of *triacetylgallic* [3:4:5-*triacetoxybenzoic*] *anhydride*, m. p. 175—176° (corr.); are formed as well. Pyridine and acetic anhydride may also be used. The acid has m. p. 171—172° (corr.), crystallises well, and forms a sparingly soluble silver salt and dark blue *copper* salt. The *chloride* is obtained in well-developed prisms, m. p. 106—107° (corr.), by the action of phosphorus pentachloride. The acid is hydrolysed to 3:5-*diacetylgallic* [3:5-*diacetoxy-4-hydroxybenzoic*] *acid*, $C_{11}H_{10}O_7,H_2O$, stout spikelets, m. p. 174—175° (corr.), by dissolving it in the required quantity of concentrated potassium hydrogen carbonate solution, and slowly adding cold 2N-sodium hydroxide (1¼ mols.), the mixture being kept below 0° and well stirred, and hydrogen being passed through without interruption. Some gallic acid and a *monoacetylgallic* [*acetoxydihydroxybenzoic*] *acid*, m. p. 225° (decomp.), are also formed, and a good deal of the triacetate escapes hydrolysis. The diacetate is methylated by means of diazomethane, the product being *methyl* 3:5-*diacetoxy-4-methoxybenzoate*, elongated tablets or prisms, m. p. 68—69°, which may be hydrolysed by cold, dilute sodium hydroxide in a current of hydrogen to the known 3:5-dihydroxy-4-methoxybenzoic

acid (gallic acid 4-methyl ether) (A., 1912, i, 559). This proves the constitution of the diacetate.

Penta-acetyl-p-digallic acid [4-(3′ : 4′ : 5′-*triacetoxybenzoyloxy*)-3 : 5-*diacetoxybenzoic acid*] is prepared by the interaction of tri-acetylgalloyl chloride and 3 : 5-diacetylgallic acid in cold, aqueous acetone in the presence of just sufficient dilute sodium hydroxide or potassium hydrogen carbonate. It forms thin needles, m. p. 202—203° (corr.), yields a *methyl ester*, m. p. 192—193° (corr.), and a *chloride*, m. p. 164—167° (corr.), and is hydrolysed by shaking with 5N-ammonia (8—9 mols.) in the cold, and in the absence of air, to *m*-digallic acid. This yields the methyl pentamethyl-*m*-digallate of definite constitution, and may also be shown not to be a para-derivative by the fact that on acetylation it yields a different penta-acetate. Penta-acetyl-*m*-digallic acid crystallises in stout prisms, m. p. 204—205° (corr.) (given in A., 1913, i, 479, as 193—194°), and forms a *methyl* ester, m. p. 167—168° (corr.). Similarly, the above methyl penta-acetyl-*p*-digallate yields *methyl* m-*digallate*, 1H_2O, m. p. 175°, when cautiously hydrolysed by ammonia. This gives a bluish-black coloration with ferric chloride, and yields precipitates with pyridine, quinoline, brucine, and quinine salts; it may also be obtained by the action of dilute ammonia on methyl penta-acetyl-*m*-digallate, or converted into this by acetylation.

3 : 5-Diacetylgallic acid is benzoylated under the same conditions as observed in the above acylation. A small amount of a *benzoyloxyacetoxybenzoic acid*, $OH \cdot C_6H_2AcBz \cdot CO_2H$, m. p. 174—176° (corr.), is formed, but the main product is the desired 4-*benzoyl*-3 : 5-*diacetylgallic* [4-*benzoyloxy*-3 : 5-*diacetoxybenzoic*] *acid* (I). This crystallises in well-developed tablets or prisms, m. p. 183—184° (corr.), forms a *methyl* ester, m. p. 138—139° (corr.), and may be hydrolysed by means of 5N-hydrochloric acid in acetic acid at 85—90°, or by ammonia at 0°, or by warming with sodium acetate, the first being the best method, to 3-*benzoylgallic* [3-*benzoyloxy*-4 : 5-*dihydroxybenzoic*] *acid* (II), which has m. p. 240—242° (corr.), and gives a bluish-green colour with ferric chloride and a deep red with potassium cyanide. When treated with diazo-methane, this yields *methyl* 3-*benzoyloxy*-4 : 5-*dimethoxybenzoate*, in stout tablets, m. p. 91—92°, which may be hydrolysed to the known 3-hydroxy-4 : 5-dimethoxybenzoic acid (3 : 4-dimethylgallic acid), m. p. 197—198° (corr.). Similarly, the above methyl 4-benzoyl-3 : 5-diacetylgallate may be converted into *methyl 3-benzoyloxy*-4 : 5-*dihydroxybenzoate*, stout plates or prisms, m. p. 173—175° (corr.), and this into the above ester, m. p. 91—92°, or into *methyl 3-benzoyloxy*-4 : 5-*diacetoxybenzoate*, elongated, flat, hexagonal tablets, m. p. 110—111°. 3-Benzoylgallic acid may also be reacetylated by means of pyridine and acetic anhydride, yielding the isomeric 3-*benzoyloxy*-4 : 5-*diacetoxybenzoic acid*, which crystallises in thin, curved needles, m. p. 177—178° (corr.), and may be esterified to the same ester as above (m. p. 110—111°), or hydrolysed again to 3-benzoylgallic acid.

4 : 5-Carbonylogallic acid (A., 1913, i, 479) yields 3-*benzoyloxy*-
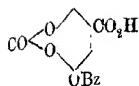
4:5-*carbonyldioxybenzoic acid* (annexed formula) when shaken with benzoyl chloride and pyridine. This crystallises in thin, hexagonal tablets, m. p. 207—210° (corr.), and is hydrolysed to 3-benzoylgallic acid by boiling with acetone and water.

DERIVATIVES OF PROTOCATECHUIC ACID.—Protocatechuic acid is most conveniently acetylated by the method used in the case of gallic acid. The diacetylprotocatechuic acid [3:4-diacetoxybenzoic acid], m. p. 157—158° (corr.), is partly hydrolysed, also by the method applied to triacetylgallic acid, the product being 3-acetylprotocatechuic acid, m. p. 202—203° (corr.), apparently identical with an acid described by Ciamician and Silber in 1892. The constitution is proved by the fact that it is converted by diazomethane into methyl 3-acetoxy-4-methoxybenzoate, m. p. 87—88°, which may be hydrolysed to 3-hydroxy-4-methoxybenzoic acid (*iso*vanillic acid). 4-*Benzoyloxy*-3-*acetoxybenzoic acid* is obtained by benzoylation, in whet-stone forms, m. p. 154—155° (corr.). This yields a *methyl* ester, m. p. 102—103° (corr.), and may be hydrolysed by means of 5*N*-hydrochloric acid mixed with acetic acid, at 100°, to 3-*benzoyloxy*-4-*hydroxybenzoic acid*. This crystallises in microscopic needles, m. p. 225—227° (corr.), and forms *methyl* 3-*benzoyloxy*-4-*methoxybenzoate*, m. p. 101—102°, when treated with diazomethane, this being also obtained by benzoylating methyl *iso*vanillate. Similarly, the above methyl 4-benzoyloxy-3-acetoxybenzoate may be hydrolysed by ammonia to *methyl* 3-*benzoyloxy-4-hydroxybenzoate*, hexagonal tablets, m. p. 153·5—155° (corr.), which yields *methyl* 3-*benzoyloxy*-4-*acetoxybenzoate*, in long, thin prisms, m. p. 54—55°, on acetylation.   J. C. W.

Phthalic Acid Derivatives. Constitution and Colour. VIII. Tetraiodofluorescein and some of its Derivatives. DAVID S. PRATT and ARTHUR B. COLEMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 236—245. Compare this vol., i, 168, 169, 170).—*Tetraiodofluorescein*, $C_{20}H_8O_5I_4$, obtainable from tetraiodophthalic anhydride and resorcinol by heating with zinc chloride, exists at the ordinary temperature as an unstable mixture of the benzenoid and quinonoid modifications. Its solutions in dilute aqueous alkali possess a yellowish-red colour and a vivid green fluorescence, and on acidification deposit a golden-yellow *hydrate*; this, when freshly precipitated, appears to contain loosely combined water, but after drying at the ordinary temperature in the air for a few days retains only approximately one molecule of water, for the removal of which a temperature of 120° is necessary; the first dehydration process does not affect the colour, but the passage into the anhydrous compound is accompanied by a change to reddish-brown, due to a partial conversion of the benzenoid into the quinonoid form; the hydrate is believed to be of the benzenoid structure. The application of a drop of acetone, alcohol, or ethyl acetate to the reddish-brown, anhydrous compound causes an immediate change of colour to a clear canary-yellow, due to rearrangement into the more stable benzenoid

modification. This behaviour is in marked contrast to that of fluorescein, which has never been isolated in the benzenoid condition. Treatment of the freshly precipitated tetraiodofluorescein with a little methyl or ethyl alcohol immediately converts it into the very pale yellow carbinol–carboxylic acid, the structural change being represented by the difference between formulæ I and II.

$$CO<^{C_6H_3(OH)}_{C_6H_3(OH)}>C<^{--O--}_{C_6I_4}>C(OH)_2$$

(I.)

$$CO<^{C_6H_3(OH)}_{C_6H_3(OH)}>C(OH)\cdot C_6I_4\cdot CO_2H$$

(II.)
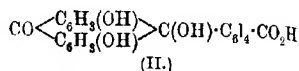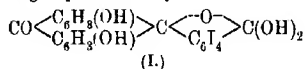
The anhydrous tetraiodofluorescein was also converted into the reddish-orange *potassium* salt, deep red *diammonium* salt, red *silver* salt, amorphous, bright red *methyl ether*, $C_{21}H_{10}O_5I_4$, decomp. near 251°, *diacetate*, $C_{24}H_{12}O_7I_4$, yellow crystals, and *dibenzoate*, $C_{34}H_{16}O_7I_4$, pale yellow crystals, m. p. 288° (corr.).   D. F. T.

Phthalic Acid Derivatives. Constitution and Colour. IX. Tetraiodoeosin and some of its Derivatives. DAVID S. PRATT and ARTHUR B. COLEMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 245—249. Compare preceding abstract).—Tetraiodofluorescein is readily brominated in acetic acid solution with formation of *tetraiodoeosin*, $C_{20}H_4O_5Br_4I_4$, canary-yellow crystals, which show no tendency to pass into a highly coloured quinonoid form, and are therefore presumably of benzenoid constitution. It dissolves in aqueous alkalis, yielding deep red solutions with faint green fluorescence, from which dilute hydrochloric acid precipitates a pink, amorphous *hydrate*, $3C_{20}H_4O_5Br_4I_4,H_2O$. Ammonia converts the solid tetraiodoeosin into a red *diammonium* salt,

$$C_{20}H_4O_5Br_4I_4,2NH_3,$$
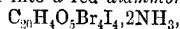
whilst the *silver* salt, $C_{20}H_3O_5Br_4I_4Ag$, obtained by precipitation, is reddish-purple. *Tetraiodoeosin methyl ether*, $C_{21}H_6O_5Br_4I_4$, obtained by the action of methyl sulphate in the presence of alkali, is a red, amorphous powder, whilst the *diacetate*, $C_{24}H_8O_7Br_4I_4$, and *dibenzoate*, $C_{34}H_{12}O_7Br_4I_4$, form pale yellow crystals, m. p. 270—280° and near 261° respectively, with liberation of iodine in both cases.   D. F. T.

Phthalic Acid Derivatives. Constitution and Colour. X. Tetraiodoerythrosin (Octaiodofluorescein) and some of its Derivatives. DAVID S. PRATT and ARTHUR B. COLEMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 249—254. Compare preceding abstracts).—*Octaiodofluorescein*, $C_{20}H_4O_5I_8$, is most conveniently obtained by heating tetraiodofluorescein with iodine and iodic acid in alcoholic solution for twelve hours. When free from combined solvent, the compound forms clear, yellow crystals, but at 140° it becomes dark red, probably due to a transformation from the benzenoid to the quinonoid constitution. With acetone, it forms a yellow *additive* compound, $C_{20}H_4O_5I_8,C_3H_6O$, which is decomposed into its con-

stituents at 120°. Gaseous ammonia converts the solid octaiodo-fluorescein into a red *tetrammonium* salt, $C_{20}H_4O_5I_8,4NH_3$, whilst the *silver* salt, $C_{20}H_8O_5I_8Ag$, obtained by precipitation, is violet. The *methyl ether*, $C_{21}H_6O_5I_8$, prepared by the action of methyl sulphate, is an unstable, dark red, non-crystalline substance, whilst the *diacetate*, $C_{24}H_6O_7I_8$, and the *dibenzoate*, $C_{34}H_{12}O_7I_8$, form yellow crystals, decomp. above 200° and m. p. near 300° respectively. D. F. T.

Phthalic Acid Derivatives. Constitution and Colour. XI. Phenoltetraiodophthalein and some of its Derivatives. DAVID S. PRATT and ASHER F. SHUPP (*J. Amer. Chem. Soc.*, 1918, **40**, 254—264. Compare preceding abstracts).—Tetraiodophthalic anhydride, yellow needles, m. p. 320—325° (corr.), obtained by heating phthalic anhydride and iodine with fuming sulphuric acid, when heated with an excess of phenol with the gradual addition of sulphuric acid, undergoes condensation with formation of phenol-tetraiodophthalein, yellow crystals, m. p. 239—245° (compare Rupp, A., 1911, i, 301), which give a deep red solution in aqueous alkali. The phthalein is probably of benzenoid constitution, the yellow colour being attributed to the influence of the iodine atoms in bringing the absorption into the visible spectrum. It yields a *diacetate*, $C_{24}H_{14}O_6I_4$, pale yellow crystals, m. p. 230° (corr.), a *dibenzoate*, $C_{34}H_{18}O_6I_4$, pale yellow needles, m. p. 236° (corr.), a *dimethyl ether*, $C_{22}H_{14}O_4I_4$, yellow crystals, m. p. 221° (corr.). a *dinitro*-derivative, $C_{20}H_6O_8N_2I_4$, yellow needles, m. p. 311—312° (corr.) (*diacetate*, $C_{24}H_{12}O_{10}N_2I_4$, deep yellow crystals, m. p. 281°, corr.), a *tetranitro*-derivative, $C_{20}H_6O_{12}N_4I_4$, yellow crystals, decomp. near 311° (corr.), and a *tetrabromo*-derivative,

$$C_{20}H_6O_4Br_4I_4,$$

yellow crystals, m. p. 311—312° (corr.) (*diacetate*, $C_{24}H_{10}O_6Br_4I_4$, yellow crystals, m. p. 285°, corr.; *dibenzoate*, $C_{34}H_{14}O_6Br_4I_4$, yellow crystals, m. p. 213—215°, corr.; *dimethyl ether*, $C_{22}H_{10}O_4Br_4I_4$, yellow crystals, m. p. 255°, corr.). By treatment in cold aqueous alkaline solution with a solution of iodine in potassium iodide it is possible to convert phenoltetraiodophthalein into *tetraiodophenol-tetraiodophthalein*, $C_{20}H_6O_4I_8$, deep yellow crystals, m. p. 285° (corr., with decomp.); this forms a *diacetate*, $C_{24}H_{10}O_6I_8$, pale yellow crystals, m. p. 288° (corr.), a *dibenzoate*, $C_{34}H_{14}O_6I_8$, pale yellow crystals, m. p. 202—203° (corr.), and a *dimethyl ether*, $C_{22}H_{10}O_4I_8$, pale yellow crystals, decomp. at 295—297° (corr.). D. F. T.

Laurent's Benzimide (Benzylidenebenzaldehydecyan-hydrin-acetal). MARIA SAVELSBERG (*J. pr. Chem.*, 1917, [ii], **96**, 186. Compare A., 1916, i, 728).—An acknowledgment of the priority of Stolle (A., 1902, i, 468) in the observation of the formation of an acetal compound by the condensation of mandelonitrile and benzaldehyde. D. F. T.

Derivatives of Veratrole. ADOLF KAUFMANN and HERMANN MÜLLER (*Ber.*, 1918, **51**, 123—130).—I. DERIVATIVES OF o-VERATR-ALDEHYDE.—2 : 3-*Dimethoxybenzyl alcohol* (o-*veratryl alcohol*) is ob-tained by reducing the aldehyde with hydrogen and platinum-black; it crystallises in very long, massive, transparent, rectangular columns, m. p. 50°, and is converted into the *chloride*, b. p. 128·5—129°/11 mm., by means of thionyl chloride. The chloride rather easily loses hydrogen chloride on distillation under higher pressures, suffering condensation to an anthracene derivative. It also combines with methylnorhydrastinine, but the normal quatern-ary chloride (I) cannot be isolated, neither can the corresponding base. The solution, however, gives precipitates of a *perchlorate* and a *picrate*, m. p. 223—225°, whilst a *benzoyl* derivative, m. p. 146°, probably of the formula II, may be obtained by the Schotten-Baumann method.

$$CH_2 \underset{O}{\overset{O}{<}} \quad \overset{CH_2}{\underset{CMe}{\underset{(I.)}{N}}} \overset{CH_2Cl}{\underset{CH_2 \cdot C_6H_3(OMe)_2}{<}}$$

$$CH_2 \underset{O}{\overset{O}{<}} \quad \overset{CH_2}{\underset{COMe}{\underset{(II.)}{NBz \cdot CH_2 \cdot CH_2(OMe)}}} \overset{CH_2}{}$$
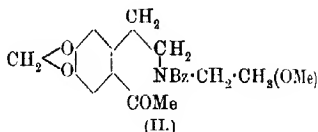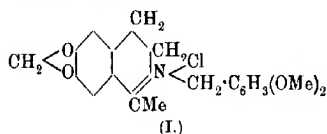
Veratraldehyde and homopiperonylamine condense to form o-*veratrylidenehomopiperonylamine*, white needles, m. p. 59—60° which may be hydrogenated in the presence of palladium-black t o-*veratrylhomopiperonylamine* (2 : 3-*dimethoxybenzyl-β-3 : 4-methyl enedioxyphenylethylamine*),

$$CH_2 \cdot O_2 \cdot C_6H_3 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CH_2 \cdot C_6H_3(OMe)_2,$$
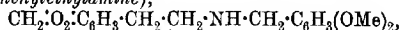
a viscous oil, which forms a *hydrochloride*, $1H_2O$.

II. p-DERIVATIVES OF VERATROLE.—p-*Homoveratronitrile* (3 : 4-*dimethoxyphenylacetonitrile*) is obtained in long, colourless needles, m. p. 64—65°, b. p. 171—178°/10 mm., by heating the correspond-ing aldoxime with acetic anhydride.

ω - Bromoacetoveratrone [3 : 4 - dimethoxyphenyl bromomethyl ketone] (Mannich and Hahn, A., 1911, i, 649) reacts with potassium acetate in boiling alcohol to form the *acetate* (glistening tablets, m. p. 91—92°) of p-*veratroylcarbinol* (3 : 4-*dimethoxybenzoylmethyl alcohol*), which separates in transparent crystals, m. p. 86—87°.

III. DERIVATIVES OF DIMETHOXYBENZOIN.—Veratrole condenses with phenylacetyl chloride under the influence of aluminium chloride to form 3 : 4-*dimethoxydeoxybenzoin* (3 : 4-*dimethoxyphenyl benzyl ketone*) in white needles, m. p. 88°. A *bromide*, pale yellow crystals, m. p. 116—117°, is produced when the required quantity of bromine is carried by a stream of carbon dioxide into a solution of this in carbon disulphide, and p-toluenesulphomethylamide reacts

with this bromide to form 3:4-*dimethoxyphenyl α-p-toluenesul-phonylmethylaminobenzyl ketone*,

$$C_6H_4Me·SO_2·NMe·CHPh·CO·C_6H_3(OMe)_2,$$

in white crystals, m. p. 180°.   J. C. W.

The Beckmann Rearrangement. VIII. Mitsuru Kuhara, Naomichi Agatsuma, and Kiukichi Araki (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1917, III, (1), *Reprint*, 16 pp.).—Kuhara and his colleagues have already shown that the esters of oximes derived from strong acids, for example, benzenesulphonates, spontaneously suffer the Beckmann rearrangement, whereas the addition of an acid like hydrochloric acid is necessary in order to bring about the change in esters of weak acids, like acetates. It is now suggested that the function of hydrochloric acid is to expel the weak acid, giving the oxime chloride which is immediately rearranged. Thus, in the case of diphenylketoxime acetate, the reaction is represented as follows: $CPh_2:N·OAc + HCl \longrightarrow MeCO_2H + CPh_2:NCl \longrightarrow CPhCl:NPh$. It is impossible to isolate these chlorine derivatives, as the reaction proceeds further to the production of benzanilide, but if the acetate is heated with benzenesulphonic acid at 95—97°, an analogous product, phenylbenziminobenzenesulphonate (A., 1915, i, 144) may be recovered, thus:

$$CPh_2:N·OAc + OH·SO_2Ph \longrightarrow MeCO_2H + CPh_2:N·O·SO_2Ph \longrightarrow$$
$$NPh:CPh·O·SO_2Ph.$$
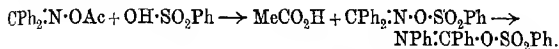
The same idea may be applied in explaining the rearrangement of the hydrochlorides of oximes under the influence of dehydrating agents. The hydrochloride of diphenylketoxime changes instantly into benzanilide when heated at 128°, quickly when heated with zinc chloride or chloral at 90°, and within a day or two at 25° when mixed with chloral. The change is formulated thus:

$$CPh_2:N·OH,HCl - H_2O \longrightarrow CPh_2:NCl \longrightarrow$$
$$CPhCl:NPh \xrightarrow{H_2O} NHPh·COPh.$$
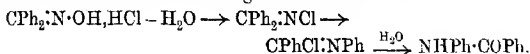
In the case of the methyl ether hydrochloride, $CPh_2:N·OMe,HCl$, methyl chloride is lost at above 45°, and no trace of the oxime suffers rearrangement, owing to the absence of the necessary :NCl group. The same interpretation is given to the rearrangement of diphenylketoxime by phosphorus pentachloride. If this agent is gradually added to an ethereal solution of the oxime, it first disappears, then the white hydrochloride of the oxime separates, and finally, when an equivalent has been added, a yellow chlorine compound is formed, which changes into benzanilide on adding water, thus: $2CPh_2:N·OH + PCl_5 \longrightarrow CPh_2:NCl + CPh_2:N·OH,HCl \xrightarrow[-H_2O]{+PCl_5}$ $CPh_2:NCl$, and this $\longrightarrow NPh:CPhCl$.

What at first sight is a weak point in Kuhara's argument is the fact that chloroiminodiphenylmethane, $CPh_2:NCl$, when prepared by the action of hypochlorous acid on iminodiphenylmethane, resists the transforming influence of a large variety of agents (compare Stieglitz and Stagner, A., 1917, i, 22). If, however, the

chloro-imine is fused with potassium hydroxide, the rearrangement takes place with almost explosive violence, aniline and benzophenone being formed. The unsubstituted imine, and also diphenylketoxime and its acetate, do not yield aniline under the same treatment. The authors' explanation is that the chlorine atom in the stable chloro-imine is positively charged, and requires to be negatively charged before spontaneous rearrangement can take place, which alteration is brought about by the molten alkali, thus: $CPh_2{:}NCl^+ \xrightarrow{KOH} CPh_2{:}NCl^- \longrightarrow NPh{:}CPhCl^-$.

Evidence is also given to show that the ease with which the oxime esters undergo rearrangement is mutually dependent on the nature of the acid radicle and the hydrocarbon residues. Thus, the following benzenesulphonates suffer rearrangement at different temperatures: $CPh_2{:}NX$, 62°; $(CH_2Ph)_2C{:}NX$, 74°; $CMe_2{:}NX$, 130°; $CMePh{:}NX$, 81—82°; $\begin{smallmatrix}OEt \cdot CPh \\ || \\ NX\end{smallmatrix}$, 95—96°; whilst the following esters of diphenylketoxime vary in stability, according to the strength of the acid: $CPh_2{:}N{\cdot}O{\cdot}SO_2Ph$, 62°;

$$CPh_2{:}N{\cdot}O{\cdot}SO_2{\cdot}C_6H_4{\cdot}NO_2(m),\ 24°;$$

$CPh_2{:}N{\cdot}O{\cdot}CO{\cdot}CH_2Cl$, above 195°; and $CPh_2{:}N{\cdot}OAc$, which does not change on heating. It appears, therefore, that the exchange of groups in the rearrangement is simultaneous.

Dibenzylketoxime benzenesulphonate (above) forms colourless crystals, m. p. 64°; the *acetate* has m. p. 33—34°, and the *benzoate*, m. p. 60·5°. *Diphenylketoxime m-nitrobenzenesulphonate* (above) has m. p. 24°, and the *chloroacetate* (above) also has m. p. 24°.

<div style="text-align:right">J. C. W.</div>

Preparation of Dihydroxyanthraquinones and their Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P., 298345, 1916; from *Chem. Zentr.*, 1917, ii, 256).—It is possible to effect the condensation of phenols, naphthols, hydroxyanthracenes, and similar substances with phthalic anhydride under the influence of aluminium chloride with production of anthraquinone derivatives in one operation if the reaction mixture is heated at approximately 180—250°; it is advantageous to use an excess of phthalic anhydride to act as solvent. In this way catechol gives hystazarin free from alizarin, in considerably greater yield than when sulphuric acid is used; a-naphthol yields pure hydroxynaphthacene-quinone, whilst β-naphthol gives hydroxynaphthanthraquinone, yellow needles. Hydroxyanthracenes and hydroxyanthraquinones reduced at the ketonic groups, for example, leucoquinizarin and deoxyalizarin, can also be condensed to hydroxyanthraquinone compounds. Pyrogallol yields anthragallol, yellow needles. The patent also refers to the formation of condensation products of phthalic anhydride with 1- and 2-hydroxyanthraquinones, 1:4:9:10-tetrahydroxyanthracene, deoxyalizarin, and 2:7-dihydroxynaphthalene. the product in the last case crystallising in yellow needles. 3:6-Dichlorophthalic acid and a-naphthol undergo condensation with

formation of a compound crystallising in brown needles and soluble in sulphuric acid to a violet solution. D. F. T.

1 : 4 : 6-**Trihydroxyanthraquinone.** M. L. CROSSLEY (*J. Amer. Chem. Soc.,* 1918, **40,** 404—406).—4-Aminophthalic anhydride (Bogert and others, A., 1902, i, 98; 1906, i, 510) condenses with quinol in concentrated sulphuric acid at 170—190° to form some 6-amino-1 : 4-dihydroxyanthraquinone (?), but chiefly 1 : 4 : 6-*trihydroxyanthraquinone,* which is a reddish-brown powder, not molten at 300°, and gives bluish-violet solutions in alkali hydroxides. It has no particular value as a mordant dye. [See also *Ind.,* April.] J. C. W.

Hydrogenation of Olefinic Terpene Alcohols, Aldehydes, and Acids. CARL PAAL (D.R.-P., 298193, 1913 ; from *Chem. Zentr.,* 1917, ii, 145—146).—Under suitable conditions it is possible to reduce alcohols, aldehydes, and acids of the terpene group by hydrogen and palladium or platinum, the ethylenic linking becoming hydrogenated, and two ethylenic linkings, if present, being capable of successive hydrogenation, without affecting the alcoholic, aldehydic, or acidic group. It is thus possible to reduce citral successively into citronellal and dihydrocitronellal; geraniol successively into citronellol and dihydrocitronellol; linalool successively into its dihydro- and tetrahydro-derivatives, and geranic acid successively into dihydrogeranic acid (*r*-citronellic acid) and tetrahydrogeranic acid. The palladium or platinum catalyst may be used in the colloidal condition, but for the present purpose the palladous or platinous hydroxide, or the metals themselves deposited on powders free from any anti-catalytic effect, are especially suited. A deposit of palladium or platinum may be formed on magnesium, nickel, or cobalt by immersing these metals in a solution of a palladium or platinum salt, or by treating precipitated magnesium oxide or carbonate or calcium carbonate with a solution of bivalent palladium or platinum it is possible to coat these powders with palladous or platinous hydroxide. Another method is to soak an indifferent powder, such as barium sulphate, infusorial earth, carbon, and cellulose powder with a solution of palladous or platinous salt, and then to precipitate the hydroxide of the rare metal on the powder by treating with sodium carbonate solution. With palladium or palladous hydroxide a convenient proportion of catalyst to carrier is 0·5—1%, whilst with platinum and its hydroxide it is 1—2%.
D. F. T.

The Colouring Matters of Camwood, Barwood, and Sanderswood. PAULINE O'NEILL and ARTHUR GEORGE PERKIN (T., 1918, **113,** 125—140).—The well-known red dye-woods, sanderswood, barwood, caliaturwood, and camwood, are very similar in tinctorial properties. In fact, the first three might well contain the same pigment, but camwood dyes mordanted wool somewhat bluer tones and is more readily extracted by water. A chemical comparison of the camwood pigment with the santalin of

sanderswood, recently investigated by Cain and Simonsen (T., 1912, **101**, 1061), appeared to be desirable, and a preliminary account of a research in this connexion is now given.

The chief, more insoluble colouring matter of camwood is found to be an isomeride of santalin, designated iso*santalin.* It decomposes at a higher temperature than santalin (250—280°, as against 250—260°) and dyes bluer shades. For many reasons, both pigments are best expressed as $C_{22}H_{18}O_6(OMe)_2$, instead of $C_{14}H_{11}O_4(OMe)$. Both woods contain more soluble dyes, which are again isomeric. For these, the names *deoxysantalin* and *deoxyisosantalin,* and the formula $C_{22}H_{16\ or\ 18}O_5(OMe)_2$, are proposed. Not much can be said as to the relation between the santalins and the deoxysantalins, except that the results of acetylation do not indicate that the former possess one more hydroxyl group than the latter. The deoxysantalins are the better pigments.

The first pigment to be isolated from sanderswood was that obtained by Meier (1848), which is apparently deoxysantalin rather than santalin, although the present authors were not so successful in obtaining a crystalline specimen. In 1870, Weidel also obtained from sanderswood, santal, which is now written as $C_{15}H_9O_5 \cdot OMe$, and a bright red substance, which is now designated *santalone,* and is possibly deoxysantalin monomethyl ether, $C_{22}H_{15}O_4(OMe)_3$. These are difficult to obtain from sanderswood, but they have now been extracted from barwood, which contains santalin as well. Santal crystallises in large, colourless leaflets, m. p. 222—223°, and yields *santol,* flat needles, m. p. 270—273°, on demethylation by Zeisel's method. Santalone forms glistening, red leaflets, m. p. 300°.

The colouring matter in the flower of St. John's wort is quercetin, and not gossypetin, as Keegan suggested (A., 1915, i, 758).

For experimental details, see the original.   J. C. W.

The Mechanism of the Formation of certain Isomerides of Cinchonine and of their Hydrohaloid Derivatives.

E. LÉGER (*Compt. rend.,* 1918, **166**, 255—258. Compare this vol., i, 121).—Admitting for cinchonine the constitution (formula I) and for cinchonigine and cinchoniline the constitu-

$$CH_2 {:} CH \cdot C_{16}H_{17}N_2 {:} CH(OH)^- \qquad CHMe \cdot [C_{16}H_{17}N_2 {:} CH]$$

(I.)   (II.)
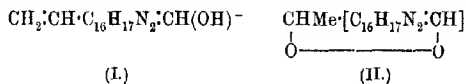
tion (formula II), and for *apo*cinchonine, $CHMe {:} C_{16}H_{16}N_2 {:} CH \cdot OH$, this latter being formed from cinchonine by the addition and subsequent removal of the elements of water, it is easy to see that the fixation of hydrogen bromide will in all four cases give the same hydrobromocinchonine. But the four compounds are optically active, and it must be supposed that the fixation of hydrogen bromide is preceded, in certain cases, by stereoisomeric changes. It is probable that cinchonine and cinchoniline have the same

teric arrangement, their isomerism being due to differences of structure. In the cases of cinchonigine and *apo*cinchonine, there s a formation of their normal hydrobromo-derivatives, and at he same time a partial transformation into cinchoniline, which hen yields hydrobromocinchonine. W. G.

A Synthesis of 2 : 6-Dimethylcinchomeronic Acid and 2 : 6-Lutidine. OTTO MUMM and HUGO HÜNEKE (*Ber.*, 1917, **50,** 1568—1584).—Some years ago, Mumm and Bergell found that he ammonium salt of acetylpyruvic acid gradually loses water to form 3-acetyl-4-methylpyridine-2 : 6-dicarboxylic acid, and this was explained on the assumption that the ammonium salt changes partly into an acid of the formula $CH_3 \cdot CO \cdot CH \vdots C(NH_2) \cdot CO_2H$, which condenses with a further portion of the salt (A., 1912, i, 936). If this view is correct, it should be possible to effect such a pyridine synthesis, using other compounds of the type of acetylpyruvic acid on the one hand, and the above unsaturated amino-acid on the other. It is now shown that ethyl acetylpyruvate and ethyl β-aminocrotonate react vigorously at 0° to form ethyl 2 : 6-dimethylcinchomeronic acid, the constitution of which is revealed by the facts that the corresponding potassium salt yields 2 : 6-lutidine on distillation with lime, and that the free acid gives an anhydride.

Ethyl acetylpyruvate, which is obtained by Claisen's method from ethyl oxalate and acetone, reacts equally well with ethyl β-aminocrotonate at 0°, whether undiluted or mixed with alcohol or ether, giving a 90% yield of *ethyl 2 : 6-dimethylpyridine-3 : 4-dicarboxylate*, which is a pale yellow, viscous oil, b. p. 163°/13 mm., m. p. 16°, and gives a *hydrochloride*, quadratic tablets, m. p. 121°, a *picrate*, clusters of stout needles, m. p. 101°, and a *platinichloride*, yellow needles. If burnt in the ordinary way, the ester apparently forms a nitrogenous compound which escapes combustion, so nitrogen was determined by Kjeldahl's method and carbon and hydrogen by Dennstedt's process. If the mixture is not cooled, the water liberated during the condensation may cause two other reactions with the parent substances, thus :

$$NH_2 \cdot CMe \vdots CH \cdot CO_2Et + H_2O = CH_2Ac \cdot CO_2Et + NH_3$$
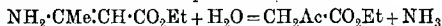
and $CH_2Ac \cdot CO \cdot CO_2Et + NH_3 = CH_2Ac \cdot C(\vdots NH) \cdot CO_2Et + H_2O$. That is, ethyl acetoacetate and *ethyl α-iminolaevulate* ("α-imide of ethyl acetylpyruvate" in the earlier paper) may be formed. The latter crystallises in thin prisms, m. p. 39°, b. p. 115°/13 mm.

The free *2 : 6-dimethylpyridine-3 : 4-dicarboxylic acid* (*2 : 6-dimethylcinchomeronic acid*) crystallises by spontaneous evaporation of aqueous solutions in short, rhombic prisms, m. p. 275° (sealed capillary; decomp.). It is almost insoluble in most solvents. The *potassium* salt forms silky needles, and gives a 91% yield of 2 : 6-dimethylpyridine (2 : 6-lutidine), b. p. 142°, when distilled with calcium hydroxide, this being at present the most convenient method for making the pure lutidine. The acid also yields an *anhydride*, needles, m. p. 101°, when heated at 220°/vac., or with acetic

anhydride. It may be that Collie and Wilsmore were correct in a tentative suggestion that they had obtained the same acid by the oxidation of 8-hydroxy-1 : 3 : 6-trimethyl*iso*quinoline (T., 1896, **69**, 295).

If the diethyl ester is left with one equivalent of alcoholic potassium hydroxide, it is partly hydrolysed to the 3-*ethyl hydrogen ester* (annexed formula), small needles, m. p. 161°, whilst the anhydride dissolves in alcohol to form the 4-*ethyl hydrogen ester*, short, flat prisms, m. p. 151°.

On heating the ammonium salt of the acid at 230°, 2 : 6-*dimethylcinchomeronimide* sublimes in very long needles, m. p. 230°.

The diethyl ester reacts with alcoholic ammonia at 120° to form the *diamide*, slender needles, m. p. 220° (heating very rapidly; vigorous decomp.). The 3-*amic acid* (annexed formula), crystallising with $2H_2O$ in rhombic leaflets, is formed by dissolving the imide in $4N$-sodium hydroxide, whilst the 4-*amic acid*, $2H_2O$, long needles, m. p. 115°, is obtained by saturating a benzene solution of the acid anhydride with ammonia.   J. C. W.
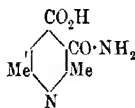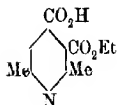
Synthesis of some Pyridine-polycarboxylic Acids. OTTO MUMM and HUGO HÜNEKE (*Ber.*, 1918, **51**, 150—164).—The synthesis of 2 : 6-dimethylcinchomeronic acid (preceding abstract) opens up a convenient way to prepare tri- and tetra-carboxylic acids of pyridine.

Oxidation of the acid with alkaline permanganate sufficient for one methyl group gives rise to a 67% yield of two methylpyridine-tricarboxylic acids. The chief product is 2-*methylberberonic acid* (2-*methylpyridine*-3 : 4 : 6-*tricarboxylic acid*), which crystallises from water in stout, short, rhombic prisms, with $3H_2O$, decomp. 226° (anhydrous), and the lesser product is 6-*methylpyridine-2 : 3 : 4-tricarboxylic acid*, which forms long, thin prisms, or sometimes hexagonal tablets, and carbonises without obvious evolution of gas at 230—280°. The two acids differ in a remarkable way in their copper salts; the former gives a precipitate with cupric acetate in hot solutions, which dissolves on cooling, but the latter gives a precipitate in the cold, which dissolves on heating.

2-Methylberberonic acid loses carbon dioxide on heating with glacial acetic acid for some days, yielding 2-*methylpyridine-3 : 4-dicarboxylic acid*, in very long, thin prisms, m. p. 250—255°, which gives an *anhydride*, m. p. 92°, when boiled with acetic anhydride, this being also formed when the tricarboxylic acid is heated at 230° in a vacuum. The new dicarboxylic acid may be oxidised by alkaline permanganate to pyridine-2 : 3 : 4-tricarboxylic acid, which crystallises in thin, rectangular leaflets, $1.5H_2O$, m. p. 249°, and is identical with the acid obtained by the oxidation of cinchonine (Camps, A., 1902, i, 824).

Both methyl groups in the original acid may be oxidised if twice as much permanganate is used. The product is pyridine-2:3:4:6-tetracarboxylic acid, which crystallises from water in narrow tablets, $3H_2O$, m. p. 235°, and is identical with the acid prepared by Fischer and Täuber from flavenol (A., 1885, 400). When this is boiled with glacial acetic acid, it loses carbon dioxide and gives a tricarboxylic acid which is not identical with any pyridinetricarboxylic acid of definite constitution, such as the above 2:3:4-acid, and can therefore only be pyridine-3:4:6-tricarboxylic acid. It is, however, crystallographically and chemically identical with berberonic acid obtained from berberine, and this synthesis confirms the structure already assigned to this acid. The acid crystallises with $2H_2O$, which it does not lose on exposure to the air, and has m. p. 243° (decomp.). J. C. W.

The Relative Stability of Cyclic Bases. V. J. VON BRAUN (*Ber.*, 1918, **51**, 96—100. Compare A., 1909, i, 604; 1911, i, 563; 1917, i, 168, 169).—Two very different methods have been worked out for effecting the rupture of cyclic systems containing nitrogen, namely, the Hofmann reaction and treatment with cyanogen bromide, but it has recently been shown that the gradations of stability exhibited by many of these bases are the same whichever test is applied. One exception seems to be dihydroindole, which proves to be one of the most stable systems in the Hofmann degradation, but one of the weakest towards cyanogen bromide.

1-Methyl-2:3-dihydroindole reacts with cyanogen bromide in the cold according to the scheme: $C_6H_4 \overset{CH_2}{\underset{NMe}{\bigg<}} CH_2 + BrCN \longrightarrow$
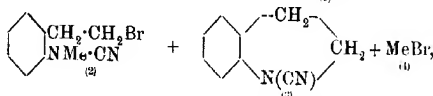
quaternary salts of (1) with (2) and (4) being formed as well, the yields being about 27% of (3) and 70% of (2), of which only 40% escapes the secondary reaction resulting in the quaternary salt. The quaternary salts are removed by ether as an insoluble, red oil, from which a small quantity of the *methobromide* of 1-methyl-dihydroindole, m. p. 195—197° (decomp.), may be recovered. The other bromide cannot be purified. The base (2) is characterised by warming the soluble products with dimethylamine dissolved in benzene, when it is converted into *cyanomethyl-o-β-dimethylaminoethylaniline*, $NMe_2 \cdot C_2H_4 \cdot C_6H_4 \cdot NMe \cdot CN$. This may be extracted from the benzene by dilute sulphuric acid; it is a pale yellow oil, b. p. 175—178°/16 mm., which exhibits pale green fluorescence in alcoholic solution, forms a *picrate*, m. p. 142°, a *platinichloride*, m. p. 144°, a *methiodide*, m. p. 170°, and may be hydrolysed by means of concentrated hydrochloric acid at 150° to *methyl-o-β-dimethylaminoethylaniline*,

$$NMe_2 \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot NHMe.$$

This base is a pale yellow oil, b. p. 138—139°/15 mm., which forms a *picrate*, m. p. 165—166°, a *platinichloride*, $2H_2O$, m. p. 218°, a *thiocarbamide*, m. p. 110°, and a *picrate* of its nitroso-derivative, m. p. 139°. The remaining product, 1-*cyano*-2:3-*dihydroindole* (3), is recovered from the above benzene solution as a yellow liquid, b. p. 164—168°/23 mm.   J. C. W.

Hydroxy-bases and Homologous Cholines. II. J. von BRAUN and Z. KÖHLER (*Ber.*, 1918, **51**, 100—108. Compare A., 1916, i, 631).—2-Methyltetrahydro*iso*quinoline forms an *ethiodide*, m. p. 132—134°, which may be converted into the hydroxide. When this is distilled under reduced pressure, the chief product is *o-vinylbenzylmethylethylamine*, which has b. p. 105—107°/17 mm., and forms a *platinichloride*, m. p. 134°, and a *methiodide*, m. p. 166—167°. The reaction,
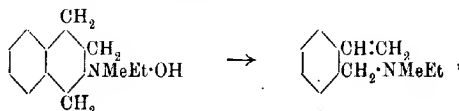
illustrates once more the instability of the tetrahydro*iso*quinoline system (A., 1917, i, 169).

N-Methyldihydro*iso*indole is formed in small quantities by the interaction of *o*-xylylene dibromide and methylamine. It has b. p. 81—82°/13 mm., and forms a *trihydrate*, m. p. 45—46°. Other derivatives were described by Fränkel (A., 1901, i, 44). The ethiodide (Scholtz, A., 1898, i, 568) may be converted into methylethyldihydro*iso*indylium hydroxide, which suffers decomposition in two ways on heating. The main product is *N*-methyldihydro*iso*indole, which is best removed by triturating the distillate with water, when the above trihydrate is formed, but *o-hydroxymethylbenzylmethylethylamine* is obtained as well, as a colourless, viscous oil, b. p. 145—150°/16 mm., which darkens on exposure to the air and gives a deep red *platinichloride*, m. p. 170°. The corresponding *dimethyldihydro*isoindylium bromide, m. p. 238—240°, from *o*-xylylene dibromide and dimethylamine, yields a hydroxide which behaves similarly on distillation. More than half of the product is *o-hydroxymethylbenzyldimethylamine*, b. p. 130—132°/13 mm., the reaction being represented thus:

$$C_6H_4{<}{CH_2 \atop CH_2}{>}NMe_2 \cdot OH \longrightarrow$$

$$C_6H_4{<}{CH_2 \atop CH_2}{>}NMe \quad \text{and} \quad C_6H_4{<}{CH_2 \cdot NMe_2 \atop CH_2 \cdot OH}.$$
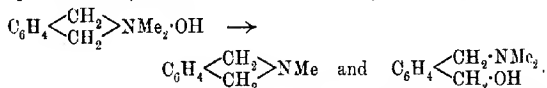
The new hydroxy-base forms an oily *picrate*, a *platinichloride*, m. p. 168°, and an oily *benzoate*, which yields a *picrate*, m. p. 159—160°, and it changes on heating with hydrochloric acid into *dimethyldihydro*isoindylium chloride, m. p. 198—200°.

The hydroxy-base may also be converted through the *methiodide*, m. p. 148—149°, into *o-hydroxymethylbenzyltri-*

methylammonium chloride, $OH \cdot CH_2 \cdot C_6H_4 \cdot CH_2 \cdot NMe_3Cl$, m. p.
189°, which has exactly the same physiological activity as choline,
and forms a *platinichloride*, m. p. 216°, and an *aurichloride*, m. p.
127°. The corresponding *allyliodide*, m. p. 123°, yields a chloride,
which, like allylhomocholine, is antagonistic to choline.

These new hydroxy-bases and *o*-hydroxymethylbenzylpiperidine
(A., 1917, i, 170) differ very characteristically from tertiary amino-
benzyl alcohols of the type $OH \cdot CH_2 \cdot C_6H_4 \cdot NMe_2$ (A., 1916, i, 473,
etc.). The former are colourless, the latter yellow, and whilst the
latter are oxidised by formaldehyde in acid solutions, the former
are quite stable towards this agent.　　　　　　　　J. C. W.

Synthesis of Cinchonic Acids. ADOLF KAUFMANN (*Ber.*,
1918, **51**, 116—122).—The cinchonic acids or their nitriles or esters
seem to be the most favourable material from which to build up
synthetic alkaloids of the cinchona group. Consequently, the
synthesis of these acids from quinolines is a matter of importance,
and therefore some new notes on the method originated by Kauf-
mann in 1909 (A., 1909, i, 958) are of interest.

The conversion of quaternary salts of the quinolines into 4-cyano-
1-alkyl-1 : 4-dihydroquinolines by means of cold, aqueous potassium
cyanide is best carried out in the presence of ether, which removes
the unstable nitrile as fast as it is formed, either by dissolving it or
by causing it to crystallise out. Quinoline itself gives a 75% yield,
but substituted bases give better results. Thus, the methosulphate
of 6-methoxyquinoline gives a very high yield of 4-cyano-6-meth-
oxy-1-methyl-1 : 4-dihydroquinoline, m. p. 82° (A., 1912, i, 651).
With the methiodides of various nitroquinolines, extremely fine
crystals of the nitrile are deposited in a very short time; 5-*nitro*-
cyano-1-*methyl*-1 : 4-*dihydroquinoline*,　$NO_2 \cdot C_6H_3 \diagdown{\substack{CH(CN) \cdot CH \\ NMe \text{---} CH}}$
separates in large, pale yellow cubes or columns, m. p. 78°
(decomp.); the 6-*nitro*-compound is a pale yellow, crystalline
powder, m. p. 108° (decomp.); and the 8-*nitro*-compound forms
large, yellow prisms, decomp. 90—92°; they all have the odour of
hydrogen cyanide and are very easily oxidised, even decomposing
with violence sometimes when brought from a desiccator into the
air.

These nitriles may be oxidised by iodine to the methiodides of
cyanoquinoline (A., 1911, i, 749, 750). This is best carried out
by dissolving the nitrile in pyridine and adding the solution quickly
to an alcoholic solution of iodine (1 mol.). The yield of the
quaternary salt varies from 90% for the unsubstituted quinoline
product to 74% for the 6-methoxy-compound and 65% for the
6-ethoxy-derivative. The corresponding nitrile from hydrastinine
and the above nitro-compounds react in a different way, being
deprived of the cyano-group and reconverted into the parent
methiodides.

The 4-cyanoquinoline methiodides are best converted into the
4-cyanoquinolines by heating alone (4-cyanoquinoline itself is

obtained in 90% yield) or with ethyl benzoate, the latter being the best treatment of the alkyloxy-derivatives.   .   J. C. W.

The Diketopiperazines. IV. Attempts to Prepare 2 : 3-Diketo-1-phenylpiperazine. J. V. DUBSKY and CH. GRÄNACHER (*Ber.*, 1917, **50**, 1686—1692. Compare A., 1916, i, 635, 672).—When an aqueous solution of 1-nitro-3 : 5-diketopiperazine ("nitroiminodiacetimide," A., 1912, i, 753) is boiled, it deposits an indigo-blue, amorphous *compound*, probably of the formula $CO{<}^{NH-CO}_{CH_2\cdot NH}{>}C\!:\!C{<}^{CO-NH}_{N(NO)\cdot CH_2}{>}CO$. This dissolves in sodium hydroxide to give a dark reddish-brown solution, which is bleached by sodium hyposulphite.

In order to obtain soluble sulphonic acids related to this insoluble product, the authors have made many attempts, described in this and in following abstracts, to prepare 2 : 3-diketo-1-phenylpiperazine, but so far without success.

In the first place, dichlorodiacetanilide, $C_6H_5\cdot N(CO\cdot CH_2Cl)_2$, was required. All attempts to prepare this from aniline and chloroacetyl chloride or chloroacetic anhydride resulted in the formation of the monochloroacetanilide, a condensation of phenylcarbimide with chloroacetic anhydride at 160—180° gave the same product mixed with 2 : 4-diketo-3-phenyltetrahydrothiazole,

$$NPh{<}^{CO\cdot CH_2}_{CO\cdot S},$$
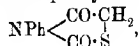
m. p. 148°.   J. C. W.

The Diketopiperazines. V. Action of Aniline on Methyl Iminodiacetate. J. V. DUBSKY and CH. GRÄNACHER (*Ber.*, 1917, **50**, 1692—1701).—In another attempt to prepare 2 : 3-diketo-1-phenylpiperazine, the authors have heated methyl iminodiacetate, or its hydrochloride, with aniline, in the hope of realising the reaction represented by equation (*a*). As a matter of fact, the reactions (*b*) and (*c*) are found to run concurrently.

(*a*) $NH(CH_2\cdot CO_2Me)_2 + NH_2Ph =$
$$NH{<}^{CH_2\cdot CO}_{CH_2\cdot CO}{>}NPh + 2MeOH.$$

(*b*) $NH(CH_2\cdot CO_2Me)_2 + 2NH_2Ph =$
$$NH(CH_2\cdot CO\cdot NHPh)_2 + 2MeOH.$$

(*c*) $2NH(CH_2\cdot CO_2Me)_2 + 2NH_2Ph =$
$$4MeOH + NHPh\cdot CO\cdot CH_2\cdot N{<}^{CO\cdot CH_2}_{CH_2\cdot CO}{>}N\cdot CH_2\cdot CO\cdot NHPh.$$
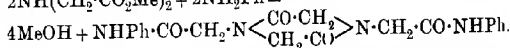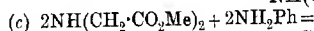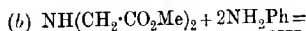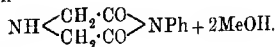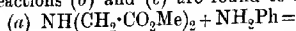
Iminodiacetonitrile (from hexamethylenetetramine and hydrogen cyanide) can be converted into methyl iminodiacetate hydrochloride in one operation (compare Jongkees, A., 1908, i, 959). 2 : 5-*Diketopiperazine*-1 : 4-*diacetanilide* (equation *c*) is not particularly soluble except in glacial acetic acid, from which it crystallises in pale grey silky leaflets, m. p. 310—320° (decomp.). On hydrolysis, it yields the known 1 : 4-diacetic acid (*ibid.*). *Iminodiacetanilide* (*b*) is extracted from the product of the reaction by means of boiling water

the mixture being slightly acidified by hydrochloric acid. It crystallises in glistening, long, snowy leaflets, m. p. 138—139°, the *hydrochloride* forms leaflets, m. p. 242° (decomp.), and the *nitrate*, stout needles, m. p. 182—183°. The salts are completely dissociated in water, but can be precipitated by the addition of the free acids or metallic salts in excess. The compound also reacts with acetic anhydride to give *acetyliminodiacetanilide*, m. p. 223—224°, and with absolute nitric acid to form *nitroiminodiacetotetranitroanilide*, $NO_2 \cdot N[CH_2 \cdot CO \cdot NH \cdot C_6H_3(NO_2)_2]_2$, which forms sulphur-yellow leaflets, m. p. 214—215° (decomp.), and dissolves in concentrated potassium hydroxide with blood-red colour.　　　J. C. W.

The Diketopiperazines. VI. Action of Bromoacetamide on Glycineanilide.

J. V. DUBSKY and CH. GRÄNACHER (*Ber.*, 1917, **50**, 1701—1709).—Glycineanilide,

$$NH_2 \cdot CH_2 \cdot CO \cdot NHPh, 2H_2O,$$
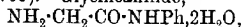
is conveniently prepared by saturating a solution of chloroacetanilide in alcohol (50 grams to 500 c.c.) with ammonia at a low temperature, heating the mixture in an autoclave at 50—60° for twelve to fifteen hours, and carefully concentrating the product. The yield is much poorer if smaller quantities are employed.

Bromoacetylglycineanilide, from bromoacetyl bromide and glycineanilide, forms slender needles, m. p. 170—172° (decomp.). It does not yield 2:5-diketo-1-phenylpiperazine when heated.

Reaction gradually sets in when equimolecular quantities of glycineanilide and bromoacetamide are mixed and left at 20°. The product is *triglycinediamideanilide*,

$$NHPh \cdot CO \cdot CH_2 \cdot N(CH_2 \cdot CO \cdot NH_2)_2,$$
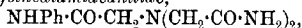
which crystallises in stout platelets, m. p. 227° (decomp.), and is not soluble in organic media. The *hydrochloride*, m. p. 200—202°, is hydrolysed by water. When heated at 200—210°/vac., the compound loses ammonia and changes into 3:5-*diketopiperazine*-1-*acetanilide*, $NH{<}^{CO \cdot CH_2}_{CO \cdot CH_2}{>}N \cdot CH_2 \cdot CO \cdot NHPh$, which crystallises in glistening leaflets, m. p. 189—190°, and forms a readily dissociated *hydrochloride*, $1H_2O$, leaflets, and *nitrate*, $0.5H_2O$, m. p. 124° (violent decomposition), whilst absolute nitric acid gives 3:5-*diketopiperazine*-1-op-*dinitroacetanilide*, very pale yellow needles, m. p. 225—226° (decomp.).

If the original glycineanilide contains iminodiacetanilide, which is usually the case, *triglycineamidedianilide*,

$$NH_2 \cdot CO \cdot CH_2 \cdot N(CH_2 \cdot CO \cdot NHPh)_2,$$
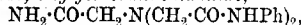
is formed as well, in the reaction with bromoacetamide. This compound is freely soluble in alcohol, and so may be extracted from the product. It crystallises in long filaments, m. p. 165°.

　　　J. C. W.

Dyes of the Anthraquinone-2 : 1-acridone Series.

FRITZ ULLMANN and PERCY DOOTSON (*Ber.*, 1918, **51**, 9—24).—Ullmann and Billig have already described the influence on the vectorial properties of anthraquinone-2:1-acridone exerted by sub-

stituents in the half of the acridine system to which the anthra-
quinone residue is attached (A., 1911, i, 489, 490). The present
communication is an outcome of an inquiry into the influence of
substituents in the other part of the acridine system. The new
derivatives are generally prepared by condensing 1-aminoanthra-
quinone with the methyl ester of a substituted o-chlorobenzoic acid,
and then treating the corresponding free o-anthraquinonylamino-
benzoic acid with concentrated sulphuric acid.

Methyl o-anthraquinonyl-1-aminobenzoate is prepared by boiling
1-aminoanthraquinone with methyl o-chlorobenzoate, potassium
acetate, and a trace of copper acetate in naphthalene solution, the
yield being 92%; it crystallises in red needles, m. p. 205° (corr.),
is hydrolysed by alcoholic sodium hydroxide to the sodium salt, and
is converted by warming with concentrated sulphuric acid, or with
sodium hydroxide and hyposulphite at 40—50°, into anthraquinone-
2 : 1-acridone. Similarly, 1 : 5-diaminoanthraquinone yields *di-
methyl o : o'-anthraquinonyl-1 : 5-diaminodibenzoate*,

$$CO_2Me \cdot C_6H_4 \cdot NH \cdot C_6H_3 {<}^{CO}_{CO}{>} C_6H_3 \cdot NH \cdot C_6H_4 \cdot CO_2Me,$$
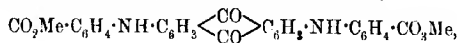
in brownish-violet, glistening crystals, m. p. 262° (corr., decomp.),
which may be converted into the corresponding acid and di-acridone
(*ibid.*).

Methyl 2-chloro-5-nitrobenzoate also condenses readily, giving an
87% yield of *methyl 5'-nitro-2'-anthraquinonyl-1-aminobenzoate*,
which crystallises in blackish-red needles, m. p. 310° (corr.), and
may be hydrolysed by *N*-sodium methoxide solution to the free
acid, orange needles, m. p. 340°. This resists condensation to an
acridone derivative, but the corresponding *5'-amino-2'-anthra-
quinonyl-1-aminobenzoic acid*, which is obtained in dark violet
crystals, m. p. 300° (decomp.), by reduction with sodium sulphide,
may be condensed by fuming sul-
phuric acid (15% SO₃) to *2'-amino-
anthraquinone-2 : 1-acridone* (annexed
formula). This crystallises in bluish-
violet tablets, decomp. 340°, and dyes
violet cotton in the vat the same shade,
whereas the unsubstituted anthra-
quinoneacridone gives reddish-violet shades.
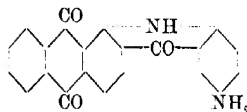
Methyl 2-chloro-5-methoxybenzoate does not react so rapidly, but
gives *methyl 2'-anthraquinonyl-1-amino-5'-methoxybenzoate*, in the
normal way. This crystallises in reddish-violet needles, m. p. 215°
(corr.), whilst the free *acid* forms a felted mass of violet needles,
m. p. 290° (decomp.), and may be converted into the chloride by
boiling with phosphorus pentachloride and benzene, and then, by
boiling with nitrobenzene, into *2'-methoxyanthraquinone-2 : 1-
acridone*. This forms small, violet leaflets, m. p. 308° (corr.), and
gives a hyposulphite vat of the same colour.

For the preparation of the 3'-methoxy-compound, *p*-methoxy-
anthranilic acid seemed to be the best starting material. This is
synthesised as follows: *p*-toluidine is converted into 2-nitro-*p*-tolu-

idine sulphate, then into 2-nitro-*p*-cresol; this is methylated by means of methyl sulphate, and the ether is oxidised by boiling with permanganate solution to 2-nitro-4-methoxybenzoic acid, which is reduced by means of stannous chloride. 4-Methoxyanthranilic acid (see also Friedländer, A., 1912, i, 318) is boiled with 1-chloroanthraquinone, potassium carbonate, and copper acetate in amyl alcohol, and so converted into *2'-anthraquinonyl-1-amino-4'-methoxybenzoic acid*, which crystallises in violet needles, m. p. 272° (decomp.), and may be transformed, through its chloride, into *3'-methoxyanthraquinone-2:1-acridone*. This forms a wine-red mass of felted needles, m. p. 350° (corr.), gives a red vat, and dyes cotton red. The influence of the substituent in the para-position with regard to the carbonyl group is therefore of the same order as Friedländer observed in the case of indigotins and " thioindigos " (*loc. cit.*), and as has been found in the case of 3'-chloroanthraquinone-2:1-acridone (D.R.-P., 245875), namely, that the shade is modified in the direction of red.

Methyl 3-chloro-2-naphthoate, m. p. 58° (for the acid, see Strohbach, A., 1902, i, 149), condenses with 1-aminoanthraquinone to form *methyl 3'-anthraquinonyl-1-amino-2'-naphthoate*, violet needles, m. p. 277°, the corresponding *acid* crystallising in violet tablets, m. p. 322°. When the ester is shaken with alkaline sodium hyposulphite at 40—50° in the absence of air it gives a vat from which air precipitates *anthraquinone-2 : 1 : 2' : 3'-naphthacridone* (annexed formula) (for the method, see D.R.-P., 246966). This crystallises in dark violet needles, m. p. 360°, and gives a green vat, from which cotton may be dyed bluish-violet. The isomeric 2:1:1':2'-anthraquinonenaphthacridone of A., 1916, i, 484, and indanthrene-red B.N. extra. of D.R.-P., 237236, dye red shades. [See also *Ind.*, 178A.]   J. C. W.
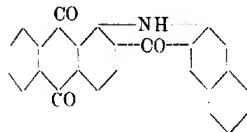
Preparation of Nitrogenous Condensation Products of the Anthraquinone Series. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 298706, 1913; from *Chem. Zentr.*, 1917, ii, 347).—Iminazole compounds of the general formula $A{<}_{-N}^{NR'}{>}CR$, where A represents an anthraquinone group possibly containing other substituents, R an aryl or alkyl radicle, and R' an aryl radicle, can be obtained in good yield with simultaneous formation of water and halogen hydracid by treating *o*-halogen substituted acylaminoanthraquinones with primary aromatic amines in the presence of neutralising agents and catalysts, such as copper salts. The products are of value for the production of dyes.

3-Bromo-1-N-phenyl-C-phenyl-1:2-anthraquinoneiminazole, prepared by heating 1:3-dibromo-2-benzoylaminoanthraquinone with aniline, potassium acetate, and copper acetate, forms yellow needles, gives an orange-red solution in sulphuric acid, and on reduction

with hyposulphite gives a vat dyeing cotton pale yellow; by warming with fuming sulphuric acid it can be converted into a sulphonic acid.   1-N-p-*Tolyl* - C- *methyl*-1 :*2-anthraquinoneiminazole*,   yellow needles, m. p. 236°, obtained similarly from 1-chloro-2-acetylamino-anthraquinone and *p*-toluidine, gives a yellow solution in sulphuric acid and a hyposulphite vat which dyes wool yellow.   D. F. T.

Chromoisomerism and Salt Formation of Iminovioluric Acids. I.   I. LIFSCHITZ and LÉON KRITZMANN (*Ber.*, 1917, 50, 1719—1738).—The bearing of residual affinity on questions of chromoisomerism and polychromism is now generally recognised, and therefore the study of a compound which can exist in tautomeric forms, and also give various internal salts by the exercise of subsidiary valencies, is of special interest. Such a compound is iminovioluric acid, which can exist, theoretically, in the following forms :—

$$CO<\!\!\begin{array}{c}NH\!\!-\!\!-\!\!CO\\NH\!\cdot\!C(NH)\end{array}\!\!>\!\!C\!:\!\overset{\displaystyle OH}{N}$$

trans.

$$CO<\!\!\begin{array}{c}NH\!\!-\!\!-\!\!CO\\NH\!\cdot\!C(NH)\end{array}\!\!>\!\!C\!:\!\underset{\displaystyle OH}{N}$$

cis.

$$CO<\!\!\begin{array}{c}NH\!\cdot\!C(OH)\\NH\!\cdot\!C(NH)\end{array}\!\!>\!\!C\!\cdot\!NO$$

Nitroso-enol.

$$CO<\!\!\begin{array}{c}NH\!\!-\!\!-\!\!CO\\NH\!\cdot\!C(NH_2)\end{array}\!\!>\!\!C\!\cdot\!NO$$
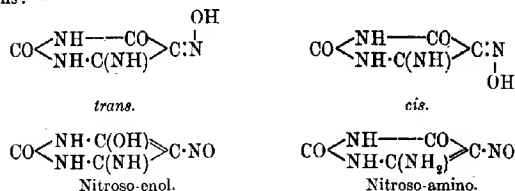
Nitroso-amino.

The isomerism in the cases of the *cis*-modification and the nitroso-amino-form would be influenced by the possibility of internal salt formation.

Iminovioluric acid is an amphoteric substance, which forms colourless salts with mineral acids and pink or red salts with the alkalis and alkaline-earths. Spectrographically, the metallic salts are identical with those of the simple violurates, which indicates that the nitroso-group is modified and involved in the establishment of a " residual affinity ring." The salts with mineral acids are optically identical with violuric acid itself, and therefore contain no residual affinity rings. The silver salt exists in a pink and a bluish-violet form, the former being most probably a salt of the above *trans*-modification, with the metallic atom linked by residual affinity to the carbonyl group, whilst the latter may be derived from the *cis*-acid, with a subsidiary valency uniting the metal and the imino-group.

The free iminovioluric acid has been isolated in three forms. The commonest is red, and spectrographically like its alkali salts; that is, it is the internally-complex form of the *cis*-modification. Another is yellowish-orange, and is to be regarded as the *trans*-isomeride, whilst the third is blue, and is most probably an internally-complex form of the nitroso-amino-type.

Some salts of iminovioluric acid were prepared by Traube in his synthesis of uric acid (A., 1900, i, 416), but the following scheme

$_{represents}$ an improved method: $CO(NH_2)_2 + CN \cdot CH_2 \cdot CO_2H$ (with $Ac_2O) \longrightarrow NH_2 \cdot CO \cdot NH \cdot CO \cdot CH_2 \cdot CN$. This

$$+ NaOH \longrightarrow CO \bigg\langle \begin{matrix} NH \text{——} CO \\ NH \cdot C(NH) \end{matrix} \bigg\rangle CH_2$$
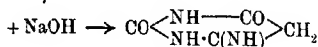
$_{nud}$ this $+ NaNO_2 + HCl \longrightarrow$ sodium hydrogen salt of iminovioluric $_{\iota}$cid, or the normal salt, according to the conditions of the reaction.

Sodium iminoviolurate, $C_4H_2O_3N_4Na$, crystallises in silky, pink $_{:l}$hreads, and the acid salt, $C_8H_7O_6N_8Na,2·5H_2O$, is reddish-violet. The *potassium* salts, obtained by similar methods, using potassium $_{:l}$itrite, are also pink and reddish-violet, but the acid salt has only $_{l}H_2O$. From the sodium salt the following new salts have been $_{\jmath}$repared: *magnesium*, $MgX_2,6H_2O$, a yellow, microcrystalline $_{\jmath}$owder, and MgX_2, a bright brick-red powder; *barium*, BaX_2,H_2O, $_{:}$ed, and $Ba_3X_2,5H_2O$, pale pink; *cupric*, $CuX_2,2H_2O$, pale green, $_{nnd}$ CuX_2, almost black; *silver*, AgX,H_2O, pink, AgX, bluish-violet, and Ag_3X,xH_2O, yellow; *strychnine*, blue; *brucine*, $BX,2·5H_2O$, yellow, BX, red, $BX,1·5H_2O$, blue; *sulphate*, $(C_4H_4O_3N_4)_2,H_2SO_4$, colourless, m. p. $140°$ (loss of water); *hydro-chloride*, $C_4H_4O_3N_4,HCl,H_2O$, unstable in the air. For the details $_{;}$f the conditions under which the various salts are formed, the $_{)}$riginal should be consulted.

Two *dimethyl* esters have also been obtained by treating the $_{:o}$dium salt with methyl sulphate; one is pale yellow and gives a $_{\gamma}$ellow solution in sodium hydroxide, the other is orange-yellow and $_{\jmath}$ives a red solution. Different ethyl esters are also formed when the different silver salts are treated with ethyl iodide.

The three forms of the free *iminovioluric acid* are obtained thus: *yellowish-orange*, by covering the sodium salt with 2- to 3-N-mineral acids; violet-tinted *red*, by exactly neutralising the sodium salt; *bluish-violet*, by boiling the others with water.

If the sodium salt is reduced with ferrous sulphate, or the free acid with iron, a very dark blue solution is obtained. In concentrated solutions, the new product may be obtained as a precipitate, which is a dark blue powder with coppery lustre. The *compound* gives a colourless solution in dilute acetic acid, from which it may be precipitated again by alkalis, and it may be represented by the formula

$$CO\bigg\langle \begin{matrix} NH \cdot CH \text{——} O \\ > C : NO \\ NH \cdot C \text{==} NH \end{matrix} \bigg\rangle Fe \cdot O \cdot Fe \bigg\langle \begin{matrix} O \text{——} CH \cdot NH \\ ON : C < \\ NH \text{==} C \text{——} NH \end{matrix} \bigg\rangle CO, 4H_2O.$$
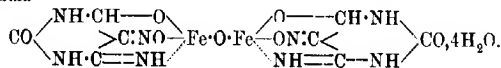
J. C. W.

Various Observations on Phenylhydrazones, Semi-carbazones, and Anils. K. von Auwers (*Ber.*, 1917, **50**, 1585—1614. Compare this vol., i, 27).

A. PHENYLHYDRAZONES.—Equimolecular proportions of 4-methyl-coumaran-2-one and *p*-nitrophenylhydrazine hydrochloride react in aqueous-alcoholic solutions in the cold to form the normal p-*nitro-phenylhydrazone* (I), which crystallises in red leaflets with metallic

green reflex, m. p. 200—204°. With an excess of the basic reagent, in boiling solutions, the coumaranone ring is opened, and the *di*-p-*nitrophenylhydrazone* of 4-*hydroxy*-m-*tolylglyoxal* (II) is formed, in dark reddish-violet leaflets, m. p. 276°.

$$C_6H_3Me\langle\begin{array}{c}C{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2\\CH_2\end{array}\rangle_O \quad\longrightarrow\quad Me\Big|\begin{array}{c}C{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2\\CH{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2\\OH\end{array}$$

(I.)   (II.)
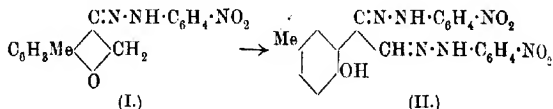
1:4-Dimethylcoumaran-2-one and *p*-bromophenylhydrazine combine without the elimination of water, the product being most probably the p-*bromophenylhydrazone* of 1-*hydroxy*-1:4-*dimethyl-coumaran-2-one*, since it is a pale yellow powder which is not soluble in sodium hydroxide. With 1-ethoxy-1:4-dimethylcoumaranone and the same base in boiling alcohol, rupture of the ring takes place to a certain extent, for the *di*-p-*bromophenylhydrazone* of 4-*hydroxy*-m-*tolyl methyl diketone*, pale yellow, flat needles, m. p. 148—149°, is formed as a by-product (compare formula II or IV).

The reaction between 1:4-dimethylcoumaran-2-one and *p*-nitrophenylhydrazine is somewhat complicated. In the main, the ring is opened and an osazone is formed, but the mother liquors from this contain the p-*nitrophenylhydrazone* of 1-*hydroxy*-1:4-*dimethylcoumaran-2-one* (III), which forms rosettes of orange-yellow needles, m. p. 171—172°. The osazone, 4-*hydroxy*-m-*tolyl methyl diketone di*-p-*nitrophenylhydrazone*, (IV), is produced from 1:4-dimethylcoumaranone, or 1-hydroxy- or 1-ethoxy-1:4-dimethyl-coumaranone by heating with *p*-nitrophenylhydrazine hydrochloride in glacial acetic acid. It crystallises in flat needles, of the appearance of chromic oxide, m. p. 255—265° (according to the rate of heating).

$$Me\Big|\begin{array}{c}C{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2\\CMe{\cdot}OH\\O\end{array}\qquad Me\Big|\begin{array}{c}C{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2\\CMe{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2\\OH\end{array}$$

(III.)   (IV.)
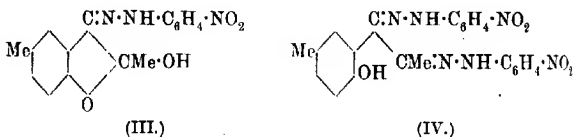
If a solution of this osazone in acetone is diluted with water or allowed to evaporate, a salmon-coloured precipitate, which looks like clean copper in the mass, is formed. This is a "*hydrate*," the elements of water being attached at one of the –C:N– groups; it has m. p. 273—274°, and loses water again if boiled with aromatic hydrocarbons or glacial acetic acid, but not by heating alone at 130°. A different "*hydrate*" is formed if the reaction between 1:4-dimethylcoumaranone and *p*-nitrophenylhydrazine is carried out in cold or boiling alcohol, or if 1-hydroxy-1:4-dimethyl-coumaranone is treated with the base in boiling alcohol; this isomeride is of a bright brick-red colour, has m. p. 265—270°, and may be dehydrated more readily. A pale brick-red "*dihydrate*"

is also formed from 1-hydroxy-1:4-dimethylcoumaranone in the cold.

The colour and stability of these "hydrates" seem to depend considerably on the mode of preparation. From the analytical data, it appears that the osazone has a tendency to hold water and aromatic hydrocarbons more or less firmly, not only in chemical but also in mechanical union. It is remarkable that, of all the coumaranones, only the 1:4-dimethyl- (and 1-hydroxy-1:4-dimethyl-) compound yields these hydrates of osazones. 1-Hydroxy-1:4-dimethylcoumaran-2-one can also be converted into a normal *p-bromophenylhydrazone*, golden-yellow prisms or brilliant, sulphur-yellow needles,, m. p. 149°, and a normal *p-nitrophenylhydrazone*, slender, sulphur-yellow needles or amber-coloured, stout prisms, m. p. 176—177°.

In other cases, normal hydrazones are formed or osazones, after opening of the ring, but it frequently happens that the latter are dimorphic. Thus, 4-methyl-1-ethylcoumaran-2-one gives the *di-p-nitrophenylhydrazone* of *4-hydroxy-*m-*tolyl ethyl diketone*, in orange-red needles, with blue reflex, m. p. 248—249°; occasionally, chromic oxide coloured leaflets or flat needles, possibly a "hydrate," were obtained. 4-Methyl-1-*iso*propylcoumaranone yields the *di-p-nitrophenylhydrazone* of *4-hydroxy-*m-*tolyl* iso*propyl diketone*; deep orange-red crystals from much methyl alcohol, and stout, yellow prisms from glacial acetic acid, m. p. 254—255°. The difference in colour between the osazones of the ethyl and *iso*propyl tolyl diketones is remarkable. 1:3:5-Trimethylcoumaran-2-one forms a normal p-*nitrophenylhydrazone*, in orange-red needles and scales, m. p. 214—215°, when treated with the base in cold alcohol, and the di-*p*-nitrophenylhydrazone of *5-hydroxy-*m-*xylyl-4-methyl diketone* (annexed formula),

$$CH_3 \cdot C\colonN\cdot NH\cdot C_6H_4\cdot NO_2$$
$$CMe\colonN\cdot NH\cdot C_6H_4\cdot NO_2$$
$$CH_3 \quad OH$$

deep ruby-red needles, m. p. 281°, in hot solutions.
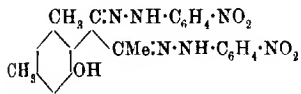
The *p*-nitrophenylhydrazone of benzaldehyde yields an *acetyl* derivative,

$$CHPh\colonN\cdot NAc\cdot C_6H_4\cdot NO_2,$$

small, pale yellow needles, m. p. 174—175°, when treated with acetyl chloride, and the *triacetate*, $OAc\cdot CHPh\cdot NAc\cdot NAc\cdot C_6H_4\cdot NO_2$, colourless scales, m. p. 154—155°, when warmed with acetic anhydride and a trace of concentrated sulphuric acid.

B. SEMICARBAZONES.—In this section, some cases of "hydrates" of semicarbazones are described.

1:4-Dimethylcoumaran-2-one suffers rupture of the ring when warmed with semicarbazide at 40—50°, the product being *4-hydroxy-*m-*tolyl a-semicarbazidoethyl ketone semicarbazone* (I),

$$C\colonN\cdot NH\cdot CO\cdot NH_2$$
$$Me \quad CHMe\cdot NH\cdot NH\cdot CO\cdot NH_2$$
$$OH$$

(I.)

$$C_6H_3Me\cdot OH$$
$$C(OH)\cdot NH\cdot NH\cdot CO\cdot NH_2$$
$$CHMe\cdot NH\cdot NH\cdot CO\cdot NH_2$$
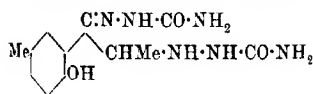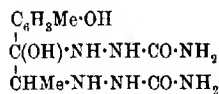
(II.)

m. p. 227°. This is precipitated as a " *hydrate* " (II), m. p. 227°
if its alkaline solutions are acidified.

1-Hydroxy-1 : 4-dimethylcoumaranone yields products, m. p
207—210° and 227—228°, which give analytical results between the
values for the true disemicarbazone of 4-hydroxy-*m*-tolyl methy
diketone and its monohydrate. 4-Methyl-1-ethylcoumaranone
gives *4-hydroxy-*m-*tolyl α-semicarbazidopropyl ketone semicarb
azone*, glassy, flat needles and rhombic plates, m. p. 230° (quickly
heated; compare also this vol., i, 29), and its "*hydrate*," m. p.
160°. Phenyl methyl diketone forms a normal *disemicarbazone*,
m. p. 229—232°.

C. ANILS.—Whilst anils show little tendency to combine with
water to form "hydrates" of the type OH·CHR·NHR′, they do
sometimes unite with acetic acid to form compounds of the type
OH·CHR·NAcR′. Some new examples are now given.

5-Nitrosalicylaldehyde yields *5-nitrosalicylideneaniline*, yellow
needles, m. p. 133°, which reacts with boiling acetic
anhydride to form the *compound*,

$$OAc·C_6H_3(NO_2)·CH(OH)·NPhAc,$$
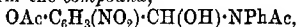
colourless needles, m. p. 145°. *5-Nitro-4-hydroxy-*m-*tolylidene-
aniline*, orange-red, flat needles, m. p. 133·5—134·5°, forms an
aniline salt, stout, ruby-red prisms, and reacts with acetic anhydride
to give the *compound*, $OAc·C_6H_2Me(NO_2)·CH(OH)·NPhAc$, white
platelets, m. p. 167°. *5-Nitro-2-hydroxy-*m-*tolylideneaniline*,
golden-yellow needles, m. p. 176—177°, forms a *diacetate*, isomeric
with the last, in glistening scales, m. p. 153—154°. J. C. W.

**Diaryl-substituted Hydrazidinecarboxylic Esters and their
Hydrolytic Products. Degradation of Ethyl Acetoacetate
to Derivatives of Formic Acid.** CARL BÜLOW and RICHARD
HUSS (*Ber.*, 1918, **51**, 24—42).—The hydrolytic degradation, and
other reactions, of the hydrazidinecarboxylates derived from ethyl
acetoacetate (this vol., i, 42) have been studied in order to confirm
the constitution assigned to them. Ethyl α-o-toluidinoglyoxylate
2 : 4-dichlorophenylhydrazone,

$$C_6H_3Cl_2·NH·N:C(NH·C_6H_4Me)·CO_2Et,$$

has been chosen for the purpose, as the possible products offer few
difficulties in the way of identifying them.

I. *Proof of the Carbethoxyl Group.*—The ester is converted by
contact with alcoholic ammonia into *α-o-toluidinoglyoxylamide
2 : 4-dichlorophenylhydrazone*,

$$C_6H_3Cl_2·NH·N:C(NH·C_6H_4Me)·CO·NH_2,$$

which crystallises in small needles, m. p. 152°, dissolves without
change in concentrated sulphuric acid, and changes into a golden-
yellow solid, with evolution of gas, if heated above its m. p. The
same amide may be formed by melting the 2 : 4-dichlorophenyl-
hydrazone of α-chloroglyoxylamide (A., 1913, i, 911) with
o-toluidine.

The ester may also be converted into the 2 : 4-*dichlorophenyl-
hydrazone* of *α-o-toluidinoglyoxylhydrazide*,

$$C_6H_3Cl_2·NH·N:C(NH·C_6H_4Me)·CO·NH·NH_2,$$
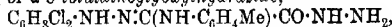
which crystallises in prisms, m. p. 145°, and condenses with aldehydes and ketones in the normal way. The iso*propylidene* compound, $C_6H_3Cl_2\cdot NH\cdot N{:}C(NH\cdot C_6H_4Me)\cdot CO\cdot NH\cdot N{:}CMe_2$, from acetone, forms slender needles, m. p. 202°, and reacts with chlorine in cold alcoholic suspension to give 2:4-dichlorophenyldiazonium chloride, which later on suffers decomposition in some inexplicable manner. The *benzylidene* compound crystallises in glistening needles, m. p. 176°, and also gives 2:4-dichlorophenyldiazonium chloride when treated with chlorine, the product yielding a crystalline, yellowish-red dye with β-naphthol. The o-*chlorobenzylidene* compound has m. p. 198°, and apparently does not give a diazonium salt if treated with chlorine in ethereal suspension. The *salicylidene* compound forms glistening, yellow needles, m. p. 186°, and is not attacked by chlorine in light petroleum. The m-*nitrobenzylidene* compound forms glistening, pale golden-yellow needles, m. p. 229°. Ethyl diacetylsuccinate also condenses with the hydrazide, giving the 2:4-*dichlorophenylhydrazone* of *ethyl* 1-α-o-*toluidinoglyoxylamido*-2:5-*dimethylpyrrole*-3:4-*dicarboxylate*,

$$\begin{matrix} C_6H_3Cl\cdot NH\cdot N \\ C_6H_4Me\cdot NH \end{matrix}\!\!>\!\!C\cdot CO\cdot NH\cdot N\!\!<\!\!\begin{matrix} CMe{:}\underset{|}{C}\cdot CO_2Et \\ CMe{:}C\cdot CO_2Et \end{matrix}'$$

in white needles, m. p. 225°, which yields a diazonium salt with chlorine.

II. *Action of Acetic Anhydride.*—The compound readily yields an *acetyl* derivative, $C_{19}H_{19}O_3N_3Cl_2$, in colourless plates, m. p. 115°, which is also converted into a diazonium salt by chlorine.

III. *Degradation to the Hydrazidine of Formic Acid.*—The ester is wetted with alcohol and warmed with 20% potassium hydroxide at 95° for a few minutes, when a new potassium salt separates, which is dissolved in warm water and mixed with hydrochloric acid. Free α-*toluidinoglyoxylic acid* 2:4-*dichlorophenylhydrazone* separates as a lemon-yellow mass, which becomes dark brown in time, even in a well-closed bottle, and gives golden-yellow solutions in most solvents. It has m. p. 98°, but if kept at this temperature in an evacuated vessel, it soon loses carbon dioxide and changes into o-*toluidinoformaldehyde* 2:4-*dichlorophenylhydrazone*,

$$C_6H_4Me\cdot NH\cdot CH{:}N\cdot NH\cdot C_6H_3Cl_2,$$
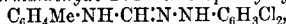
which forms white needles, m. p. 91°.

IV. *Complete Disruption.*—The ester is decomposed by warming with zinc dust and glacial acetic acid into 2:4-dichloroaniline and o-toluidine, this being identified by removing the solid base as far as possible and converting the oil into o-tolueneazo-β-naphthol. The ester may be recovered almost entirely unchanged after boiling with water for a week, but it is hydrolysed by boiling hydrochloric acid, yielding 2:4-dichlorophenylhydrazine, m. p. 90°, oxalic acid, and o-toluidine. J. C. W.

Hydrazides and Azides of Sulphocarboxylic Acids. ERNST SCHRADER (*J. pr. Chem.*, 1917, [ii], **96**, 180—185).—When hydrazine and o-cyanobenzenesulphonyl chloride react in benzene solution, the product is a heterocyclic compound, o-*sulphohydrazido*-

benzohydrazide anhydride, $SO_2 \!\! <^{NH \cdot N}_{C_6H_4} \!\! > C \cdot NH \cdot NH_2$, needles, m. p.
154° (decomp.), which with benzaldehyde yields a *benzylidene*
derivative, $C_{14}H_{12}O_2N_4S$, prisms, m. p. 179°. With aqueous sodium
azide, an ethereal solution of *o*-cyanobenzenesulphonyl chloride
slowly reacts with formation of *o-cyanobenzenesulphonylazide*,
$CN \cdot C_6H_4 \cdot SO_2 \cdot N_3$, non-explosive rhombohedra, m. p. 40°.

D. F. T.

**Compounds Derived from Proteins by Energetic Treat-
ment with Nitric Acid. VI.** CARL TH. MÖRNER (*Zeitsch.
physiol. Chem.*, 1917, **101**, 15—24. Compare A., 1917, i, 711).—
The ethereal extract of the products of the action of nitric acid
on proteins yields, on fractional crystallisation from hot water,
benzoic and *m*-nitrobenzoic acids, both of which are probably
formed from the aromatic amino-acids in the protein.

From the aqueous extract of the precipitate formed by the addi-
tion of barium hydroxide and alcohol to the hydrolysed protein
solution (compare A., 1915, i, 324), shining, yellow prisms separate
after some days, from which, on treatment with dilute nitric acid,
an *acid substance*, $C_4H_3O_4N_3$, is liberated which melts at about
300°. It appears to be a derivative of glyoxaline.

During the extraction of the products of the action of nitric
acid on hæmoglobin by ether, a yellow powder gradually settles
out from the originally clear liquid. On recrystallisation, an *acid
substance* is obtained in small, colourless, polygonal crystals,
$C_5H_3O_3N_2$, m. p. about 300°.

Among the products of the combined action of hydrochloric and
nitric acids on gluten, a substance was isolated which crystallised
in slender needles, but appeared, nevertheless, to be a mixture of
chlorinated benzoic acids.   H. W. B.

**Effects of Electrolytes on Gelatin and their Biological
Significance. I. Effects of Acids and Salts on the Pre-
cipitation of Gelatin by Alcohol.** W. O. FENN (*J. Biol.
Chem.*, 1918, **33**, 279—294).—The author finds that the quantity
of alcohol required to precipitate a fixed amount of gelatin from
its solution is dependent on the nature and number of ions present
in the gelatin solution. The method consists essentially in adding
95% alcohol to 5 c.c. of the gelatin–electrolyte mixture in a test-
tube until such an opacity is produced that a pencil held behind
the test-tube can no longer be seen. The number of c.c. of alcohol
added constitutes the "alcohol number."

The results show that acids, alkalis, and salts hinder the pre-
cipitation of gelatin by alcohol. In the case of strong acids and
alkalis, this effect rapidly increases, passes through a sharp maxi-
mum, and then decreases as the concentration of the electrolyte is
increased. Thus, when the conditions above described are observed,
the quantity of alcohol required to precipitate the gelatin rapidly
increases as the concentration of hydrochloric acid in the gelatin
solution is raised from 0 to $0.024M$. From 0.024 to $0.095M$, pre-
cipitation does not occur, however much alcohol is added, whilst

beyond this limit the amount of alcohol required slowly diminishes. When salts are added, the precipitation of the gelatin is also hindered, and the effect becomes more marked as the concentration of the salt is increased. Tervalent ions are more effective than bivalent, and bivalent than univalent in this respect. Certain salts, such as aluminium and copper chlorides, which are very effective in hindering precipitation by alcohol, resemble the strong acids in that their effect passes through a maximum and then decreases. Others, such as manganese sulphate, containing bivalent cations and anions, are exceptions to the general rule, and either assist or only very slightly hinder the precipitation of gelatin by alcohol. The effect of the sulphates, citrates, and tartrates of the alkali metals decreases in high concentrations, due to their strong "salting out" or dehydrating powers. Eventually a point is reached where the salt itself precipitates the gelatin without any addition of alcohol being required. The discussion of the theoretical significance of these results is reserved for a future communication. H. W. B.

Action of Diazomethane on Hæmin. WILLIAM KÜSTER [with OTTO GEERING and O. KUSCH] (*Zeitsch. physiol. Chem.*, 1917, 101, 25—32. Compare A., 1915, i, 853).—It has been stated (*loc. cit.*) that whereas bilirubin and hæmatoporphyrin are readily esterified by diazomethane, hæmin is only esterified with difficulty or not at all. Further experiments have shown that only a very small percentage of α-chlorohæmin is esterified by diazomethane, whilst α-bromohæmin is quite unattacked. On the other hand, some β-hæmin derivatives have been found to be readily methylated by this reagent. β-Bromoethylhæmin is converted into β-methylethylhæmin and β-chlorohæmin into β-chloromethylhæmin; but β-chloromethylhæmin is unattacked, and in mixtures containing β-chlorohæmin and the methyl mono-ester, only the β-chlorohæmin undergoes methylation. The methylation of the second carboxyl in β-hæmin can therefore only occur through the agency of diazomethane when the first carboxyl has been esterified by the ethyl radicle, and hence it follows that the carboxyl esterified by ethyl alcohol is different from that esterified by methyl alcohol. These results furnish new evidence for the view that the carboxyl radicles in hæmin are affected in different ways by the neighbouring basic and iron-containing groups (compare A., 1912, i, 670), one being in closer relation to the basic group than the other. This is illustrated by the scheme:

$$COO \cdot NH + MeOH \longrightarrow COO \cdot NH \text{ not methylated by diazomethane}$$
$$CO_2H \qquad\qquad CO_2Me$$

$$COO \cdot NH + EtOH \longrightarrow COO \cdot NEt \text{ methylated forming } COO \cdot NEt$$
$$CO_2H \qquad\qquad CO_2H \qquad\qquad CO_2Me$$
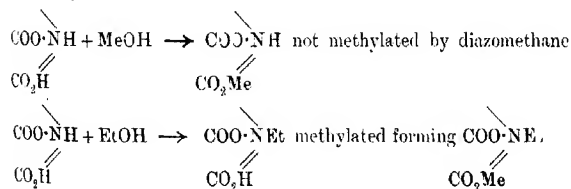
β-*Bromoethylhaemin*, $C_{36}H_{36}O_4N_4BrFe$, prepared by Mörner, method, when suspended in chloroform and treated with diazo-methane, yields β-*bromomethylethylhaemin*, $C_{37}H_{38}O_4N_4BrFe$, which is insoluble in 5% sodium carbonate solution.   H. W. B.

Esterification and Empirical Composition of Hæmin.

WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1917, **101**, 33—42 Compare preceding abstract).—Hæmin prepared by Mörner's method, using pure ethyl alcohol, consists of a mixture of α-hæmin and monoethylhæmin, whilst when methyl alcohol is employed, the products consist of β-hæmin, monomethyl-, and dimethyl-hæmin. When a mixture of ethyl and methyl alcohols is used, methylhæmin is first formed, which then interacts with the ethyl alcohol to form ethylhæmin. Since it has been shown (*loc. cit.*) that ethyl and methyl alcohols become attached to different carboxyl groups, it follows that the ethylhæmin formed by the direct action of ethyl alcohol on hæmin should be isomeric with that formed by the action of the mixture of alcohols in which the ethylhæmin is produced from the primary methylhæmin. Experiments carried out on these lines have not been so far successful in isolating two isomeric ethyl-hæmins, only mixtures of mono- and dialkyl-hæmins being obtained.

The analyses of the alkyl- and halogen-hæmins prepared in various ways are all in harmony with the empirical formula $C_{34}H_{32}O_4N_4Cl(Br)Fe$ for hæmin.   H. W. B.

Action of Aniline on Hæmin and its Transformation by the Acetic Acid Method.

WILLIAM KÜSTER [with, in part, LOBMILLER] (*Zeitsch. physiol. Chem.*, 1917, **101**, 43—76. Compare A., 1914, i, 887, and preceding abstracts).—The product of the action of aniline on hæmin consists of a mixture of three substances. One of these, hydroxyhæmin, is formed from chloro- or bromo-hæmin by the probable intermediate production of an additive compound of the hæmin with aniline, which subsequently undergoes hydrolysis. It acts as a base, forming salts with acids and has the hydroxyl group attached directly to the iron atom in the hæmin molecule. The other two products are two dehydro-halogenohæmins, in one of which the iron atom is attached to oxygen and in the other to nitrogen. The latter N-derivative is more stable than the O-derivative, and therefore does not so readily undergo transformation into a true hæmin. By the action of aniline on β-chloromethylhæmin, N-dehydrochlorohæmin and hydroxyhæmin are formed, of which only the latter yields crystalline β-dimethylhæmin when esterified by means of methyl alcohol and hydrogen chloride.

Two α-dehydrobromohæmins are similarly produced by the action of aniline on α-bromohæmin, and can be separated by treating with a pyridine–chloroform mixture. Part dissolves, but the solution does not yield hæmin when poured into acetic acid containing sodium chloride. The insoluble portion dissolves in alcoholic ammonia, and is readily converted into crystallised hæmin. In the first case, the iron atom is attached to nitrogen, whilst in the

second the less stable iron–oxygen compound is present, which is therefore transformable into hæmin.

In some cases, the failure to re-form a crystalline hæmin from a methylated hæmin is ascribed to the intermediate production of a "pseudohæmin," in which salt formation with one of the basic nitrogen atoms is assumed to occur. · H. W. B.

The Influence of Neutral Salts on the Action of Urease. J. TEMMINCK GROLL (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 559—565).—The cations exert a preponderating influence on the decomposition of carbamide by urease, the anions having comparatively little influence. The cations and the anions, in so far as the influence of the latter can be observed, arrange themselves, as regards their retarding action on urease, in much the same order as they do in regard to their influence on various colloidal phenomena. W. G.

Physiological Chemistry.

Respiratory Regulation of the Carbon Dioxide Capacity of the Blood. I. High Levels of Carbon Dioxide and Alkali. YANDELL HENDERSON and H. W. HAGGARD (*J. Biol. Chem.*, 1918, **33**, 333—344).—The authors describe experiments on dogs which show that when, by means of subcutaneous injections of morphine, respiration is depressed and the alveolar carbon dioxide is raised, or when, by the administration of carbon dioxide in the air breathed, the carbon dioxide content of the blood is raised above the normal level, the "carbon dioxide capacity" or "alkaline reserve" (Van Slyke and Cullen, A., 1917, i, 521) of the blood also rises. This rise is probably due to a compensatory passage of alkali from the tissues into the blood. Through this mechanism, respiration exerts a powerful influence on the alkaline reserve of the blood. H. W. B.

Respiratory Regulation of the Carbon Dioxide Capacity of the Blood. II. Low Levels of Carbon Dioxide and Alkali induced by Ether. Their Prevention and Reversal. YANDELL HENDERSON and H. W. HAGGARD (*J. Biol. Chem.*, 1918, **33**, 345—353. Compare preceding abstract).—The disturbance of the alkaline reserve or (as the authors prefer to call it) the carbon dioxide capacity of the blood by administration of ether appears from these experiments to be wholly dependent on disturbance of respiration. If the anæsthesia is managed so that respiration is but little increased, the lowering of the alkaline reserve of the blood is slight. When, however, respiration is simultaneously

excited, the alkaline reserve may be greatly reduced. Down to a certain critical level, recovery may spontaneously ensue, but below this level the changes appear to become irreversible, resulting in the death of the animal. Light anæsthesia loses its harmful tendencies when sufficient carbon dioxide is administered to maintain the alveolar carbon dioxide at the normal level. It follows that, in ether anæsthesia, the alkaline reserve or carbon dioxide capacity of the blood is determined and controlled by its carbon dioxide content, which is in turn dependent on the alveolar carbon dioxide, or eventually on the respiration.

· When the ether anæsthesia is so profound as to depress respiration, a rise occurs in the alkaline reserve of the blood.

H. W. B.

Respiratory Regulation of the Carbon Dioxide Capacity of the Blood. III.   The Effects of Excessive Pulmonary Ventilation. YANDELL HENDERSON and H. W. HAGGARD (*J. Biol. Chem.*, 1918, **33**, 355—363. Compare preceding abstracts).—The authors describe experiments on dogs which show that excessive pulmonary ventilation by means of artificial respiration induces not only a lowering of the carbon dioxide content, but also of the alkaline reserve of the blood. The arterial pressure also falls, and death may follow. If the artificial respiration, instead of being made with fresh air, is carried on by continual reinjection mainly of expired air, so that the carbon dioxide content of the blood is not reduced, the alkaline reserve and arterial pressure do not fall and the other ill-effects also fail to appear.   H. W. B.

Respiratory Regulation of the Carbon Dioxide Capacity of the Blood. IV.   The Sequence of Trauma, Excessive Breathing, Reduced Carbon Dioxide Capacity, and Shock. YANDELL HENDERSON and H. W. HAGGARD (*J. Biol. Chem.*, 1918, **33**, 365—371. Compare preceding abstracts).—The experiments show that trauma does not cause a lowering of the carbon dioxide capacity or alkaline reserve of the blood if measures are taken to prevent excessive pulmonary ventilation. Beneficial results may therefore be expected to attend the administration of carbon dioxide to wounded soldiers with the view of the prevention of "shock."

H. W. B.

The Occurrence of Creatine and Creatinine in the Blood in Normal and Pathological Conditions. II.   In Young Individuals : Method of Estimation. JOH. FEIGL (*Biochem. Zeitsch.*, 1917, **84**, 264—280).—The creatinine content of blood in children up to fifteen years of age is smaller than is that of adult men. The author confirms the value of Folin's method for estimating creatinine, especially the modification of Folin and Doisy, and rejects the .unfavourable criticisms of MacCrudden and Sargent. Attention is directed to the necessity of employing pure reagents.   S. B. S.

The Physical Chemistry of the White Corpuscles and Pus.

F. TANGL and K. BODON (*Biochem. Zeitsch.*, 1917, **84**, 183—193). —Measurements of the electrical conductivity of the whole pus, serum, and leucocytes. The conductivity of the last-named is least. If these are diluted with water, the conductivity diminishes progressively with the dilution, and in this respect they differ from erythrocytes, of which the conductivity progressively increases on dilution up to a certain point, beyond which further addition of water causes a diminution of conductivity. S. B. S.

Phosphates in Human Blood-serum. IV. Orthophosphates and Residual Phosphorus in Bright's Disease.

JOH. FEIGL (*Biochem. Zeitsch.*, 1917, **84**, 231—245).—Attention is directed to the differences in the distribution of phosphorus in the serum in cases of typical (acute) and chronic glomerular nephritis. S. B. S.

The Change in the Hydrion Concentration of Muscle during Work.

J. GOLDBERGER (*Biochem. Zeitsch.*, 1917, **84**, 201—209).—The reaction of extracts of muscular tissue (gastrocnemius of frogs) is always slightly acid when determined electrometrically. The hydrion concentration increases after muscular work. The acidity, determined by titration (to phenolphthalein), is seven to ten thousand times greater than that determined electrometrically. The increased acidity due to muscular work is caused chiefly by volatile acids, chiefly carbon dioxide. S. B. S.

The Reaction of Human Milk.

ALEXANDER SZILI (*Biochem. Zeitsch.*, 1917, **84**, 194—200).—The hydrion concentration of milk is almost exactly that of water when measured electrometrically, and does not change appreciably during the course of lactation. The milk in the later stages of lactation requires somewhat less alkali than in the earlier stages for neutralisation to phenolphthalein. S. B. S.

New Constituents of Milk. III. A New Protein, Soluble in Alcohol.

THOMAS B. OSBORNE and ALFRED J. WAKEMAN [with CHARLES S. LEAVENWORTH and OWEN L. NOLAN] (*J. Biol. Chem.*, 1918, **33**, 243—251. Compare A., 1917, i, 103).—The new protein is precipitated, together with caseinogen, when dilute hydrochloric acid is added to milk. The precipitated proteins are purified by repeatedly dissolving in dilute alkali and reprecipitating with dilute acetic or hydrochloric acid. The moist proteins are now treated with an equal volume of 92% alcohol; the new protein dissolves, and on pouring the concentrated filtrate into water, it separates in flocculent masses, which can be collected on a filter, washed, and dried over sulphuric acid. The white powder finally obtained gives the following figures: 54·91% C, 7·17% H, 15·71% N, 0·95% S, and 0·08% P. It thus contains more carbon and sulphur and less phosphorus than caseinogen. When examined by Haus

mann's method for the distribution of nitrogen, the new protein does not yield more amide-N or less basic-N than do caseinogen and other animal proteins, and in this respect does not resemble the alcohol-soluble proteins of vegetable origin, although so like gliadin in its solubility in relatively strong alcohol. That it is quite distinct from all the other proteins in milk is shown not only by its behaviour towards solvents and its chemical composition, but also by the fact that it does not react anaphylactically with any of these other proteins, although it is itself highly anaphy-lactogenic.

The alcohol-soluble milk protein possesses distinctly acid properties; it is almost insoluble in water, but dissolves in dilute alkalis. The solubility of the protein in alcohol of various degrees of concentration depends much on the temperature; it dissolves readily in warm 70% alcohol, but a small proportion separates out on cooling. It is insoluble in absolute alcohol.

Although the new protein is precipitated from its solutions by acids, it is nevertheless completely dissolved by very dilute acetic acid. On adding potassium ferrocyanide, a voluminous precipitate is produced. The protein also gives strong tryptophan, Millon's and biuret reactions. These properties distinguish it from any type of protein hitherto discovered in animal tissues or products.

H. W. B.

Mathematical Formulæ and Acid Excretion. GEORGE D. BARNETT (*J. Biol. Chem.*, 1918, **33**, 267—270. Compare Fitz and Van Slyke, A., 1917, i, 522).—The author raises a protest against the introduction of complex mathematical formulæ to express the relations existing between the various factors concerned in the excretion of urine by the kidney. It is shown that the results obtained by Fitz and Van Slyke, which were stated to be in agreement with the modification of Ambard's formula, plasma carbon dioxide $= 80 - \sqrt{D/W} . \sqrt{C}$, can be even better expressed by the simpler formula, plasma carbon dioxide $= 80 - 5\sqrt{D/W}$. Other formulæ are also put forward which express the relations between the results with a greater degree of accuracy than is attained by Fitz and Van Slyke's formula. Moreover, it is pointed out that using Fitz and Van Slyke's formula, the average deviation of "calculated" from "found" values of plasma carbon dioxide is much greater than would result if maximal additive errors occurred in all the estimations involved. H. W. B.

Acidosis. X. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1918, **33**, 271—278. Compare preceding abstract).—The author agrees that the simplified formula, plasma carbon dioxide $= 80 - 5\sqrt{D/W}$. put forward by Barnett (*loc. cit.*) expresses with the greatest degree of accuracy the relationship existing between alkaline reserve and acid excretion. The additional formulæ advanced by Barnett are shown to fail when applied in the cases of children.

H. W. B.

Physico - chemical Investigations on Experimental Uræmia. M. BIENENSTOCK and L. CSÁKI (*Biochem. Zeitsch.*, 1917, , 210—224).—Dogs were rendered uræmic either by extirpation the kidneys or by ligaturing the ureters. The following nstants of the serum were determined before and after opera- n: dry matter, ash (soluble and insoluble in water), organic tter, surface tension, refraction, viscosity, lowering of freezing int, conductivity, hydrion concentration, nitrogen, number and lume of red corpuscles. The animals were allowed food and ter after the operations, and the changes produced by the æmia were not always in the same direction. The general results em to warrant the conclusion, however, that uræmia causes an crease of the organic molecules in the serum and a diminution the inorganic; the increase of the former is larger than the minution of the latter, so that the total number of the mole- les is increased. The fact of the diminution of the inorganic olecules was confirmed by estimation of chlorine in the serum of nimals which had been deprived of food and water after the eration. The results are ascribed generally to the increase of e acidity of the serum produced by uræmia. S. B. S.

Pyruvic Acid. L. KARCZAG (*Biochem. Zeitsch.*, 1917, **84,** 25—230).—Both rats and guinea-pigs show a high tolerance to e acid. The injection produces neither hyperglycæmia, nor cretion in the urine of dextrose, lactic acid, volatile fatty acids, r pyruvic acid. The urine excreted is alkaline and contains a rge amount of carbonate.

Certain bacteria bring about the fermentation of pyruvic acid nly when grown on bouillon, but not on simpler media.
S. B. S.

Metabolic Changes induced by Administration of Guan-dine Bases. I. Influence of Injected Guanidine Hydro-chloride on the Sugar Content of the Blood. C. K. WATANABE (*J. Biol. Chem.*, 1918, **33**, 253—265).—The injection f guanidine hydrochloride into a rabbit is followed by symptoms which are almost identical with those of tetanus produced by extirpation of the parathyroid glands. It is now shown that hypoglycæmia results from the injection of guanidine hydrochloride, and since guanidine derivatives are known to appear in consider- able amounts in the blood and urine after parathyroidectomy (Koch, A., 1913, i, 935), it is probable that the hypoglycæmia observed after the experimental removal of the parathyroids in animals (Underhill and Blatherwick, A., 1917, i, 897) or in tetanus in man is a secondary effect produced by guanidine poisoning. H. W. B.

Methods of Gas Warfare. S. J. M. AULD (*J. Washington Acad. Sci.*, 1918, **8**, 45—58).—A popular chronological account of the methods used by the Germans in gas attack. The first attack

was made by chlorine in the form of a gas cloud, this being followed by the use of phosgene [carbonyl chloride]. In gas shells, various substances were used. The original "tear" shells contained almost pure xylyl bromide or benzyl bromide, but some of the shells were rendered almost inactive by the presence of 20% of the dibromide. Later, chloromethyl and trichloromethyl chloro-formates were used. They had no decided reaction on the eyes, but were highly poisonous. One of the latest substances used was dichlorodiethyl sulphide (mustard gas), which acted as a "super-lachrymator." It had no immediate action on the eyes beyond causing slight irritation, but after several hours the eyes began to swell and inflame and practically to blister, the nose discharged freely, and severe coughing and even vomiting ensued. Direct con-tact with the spray caused severe blistering of the skin. Other sub-stances used were: (1) in shells, allylthiocarbimide, bromomethyl ethyl ketone, methyl bromoethyl ketone, methyl dibromoethyl ·ketone, $CH_3 \cdot CO \cdot CHBr \cdot CH_2Br$, trichloronitromethane (chloro-picrin), $CCl_3 \cdot NO_2$, diphenylchloroarsine, $AsPh_2Cl$, dichloromethyl ether, $(CH_2Cl)_2O$, phenylcarbylamine chloride, $PhN \overset{.}{.} CCl_2$; (2) in grenades, bromoacetone, bromine, chloroacetone, chlorosulphonic acid, dimethyl sulphate, methyl chlorosulphonate, sulphur tri-oxide.

The most satisfactory absorbents used in respirators against these attacks have been: (1) a saturated solution of sodium phenoxide; (2) hexamethylenetetramine (urotropine) used in conjunction with sodium phenoxide and sodium hydroxide; (3) active absorbent charcoal; (4) the latter and alkaline permanganate.   W. G.

Chemistry of Vegetable Physiology and Agriculture.

The Formation of Phenol in the Human Intestine. M. RHEIN (*Biochem. Zeitsch.*, 1917, **84**, 246—263).—The author has succeeded in isolating an organism, which he designates as *Bacterium coli phenologenes*, from the human fæces which is cap-able of producing phenol from tyrosine. It differs in these respects from the ordinary *coli* bacillus, to which it is similar in all other respects. In the presence of sugars, which are fermented by it, it does not produce phenol. It can also produce phenol from *p*-hydroxybenzoic acid, which is thus indicated as an intermediary product in the formation of phenol from tyrosine.   S. B. S.

A Correlation between Bacterial Activity and Lime Requirements of Soils. FIRMAN E. BEAR (*Soil Sci.*, 1917, **4**, 433—462).—Pot experiments were conducted with soils having lime requirements varying from 0—0·23% of calcium carbonate,

the latter being applied in amounts ranging from 0·01—2·0% of the weight of the soil. The results indicate that the various groups of soil organisms varied in their response to applications of calcium carbonate. Ammonification proceeded fairly satisfactorily . in most of the soils as obtained, but the rate was increased, in most cases, by the addition of moderate amounts of calcium carbonate. The rate of nitrification was almost directly correlated with the amount of calcium carbonate applied, and excessive applications were not injurious to the nitrifying organisms. Nitrogen fixation by non-symbiotic soil organisms was considerably increased by the addition of calcium carbonate, but an application of monocalcium phosphate was also necessary for maximum nitrogen fixation. Nitrogen fixation accompanying the growth of soja beans took place readily in acid soils. It was increased by small applications, but decreased by large applications of calcium carbonate. A good growth of soja beans was obtained in a soil having a lime requirement of 0·15%, but well supplied with acid phosphate or manure. [See, further, *Ind.*, 188A.]   W. G.

The Assimilation of Carbon Dioxide. II. Baeyer's Assimilation Hypothesis. The Connecting Link in Carbohydrate Formation. RICHARD WILLSTÄTTER and ARTHUR STOLL (*Ber.*, 1917, **50**, 1777—1791. Compare A., 1916, i, 105).—The well-known hypothesis that formaldehyde is the connecting link between carbon dioxide and carbohydrates in the plant, first suggested by Baeyer in 1870, has often been attacked in recent years. Many experiments have been made with the object of detecting formaldehyde in the plant, but even if it were found to be present it would not prove that it had been derived from carbon dioxide, since Spoehr has shown that it may be produced by the photolysis of many vegetable acids (A., 1914, i, 120). From time to time, therefore, theories have been advanced in which other deoxidation products of carbon dioxide, such as oxalic acid and glycollic acid, have been suggested as the initial product.

On examination, it will be found that of all the possible primary products, formaldehyde is the only one in the formation of which the volume of carbon dioxide absorbed would be equal to the volume of oxygen liberated. In other words, the "assimilatory quotient," CO_2/O_2, is 1 in the case of formaldehyde, 1·33 for glycollic acid, 2 for formic acid, and 4 for oxalic acid. If it could be arranged, therefore, to determine this quotient in a trustworthy manner, eliminating respiratory effects and so forth, an answer could be given to the much-debated question.

By a method similar to that described in connexion with the assimilatory activity of leaves with different chlorophyll content (*loc. cit.*), the quotient can be determined with a high degree of accuracy, the experimental error only influencing the second place of decimals, and it is found that the quotient is unity, whether the temperature is 10° or 35°, whether the atmosphere is rich in carbon dioxide or even deprived of oxygen altogether (experiment with

cyclamen), or whether ordinary foliage or succulent leaves like cactus are examined.   · J. C. W.

An Examination of the Leaves of Adonis Vernalis. FREDERICK W. HEYL, MERRILL C. HART, and JAMES M. SCHMIDT (*J. Amer. Chem. Soc.*, 1918, **40**, 436—453).—Tincture of *Adonis vernalis*, or false hellebore, has been used in recent years in cases of cardiac dropsy and epilepsy. The activity is usually assigned to a digitalis-like glucoside, adonidin, which was first described by Cervello (A., 1882, 1126), but the drug which may be purchased under this name is prepared from the roots (Merck's Index, 1907).

The authors have now made a systematic examination of the leaves, having obtained a considerable quantity from Leipzig. They find that an extract in 95% alcohol is somewhat more toxic than digitalis tincture, the average minimum dose which induces permanent systole of the frog's ventricle at the end of one hour (M.S.D.) being about 0·0045 c.c. per gram body weight. They have failed to obtain any more than the slightest evidence of the presence of adonidin or any glucoside in the leaf, but find that more than 60% of the toxicity is connected with the basic fraction precipitated by phosphotungstic acid.

An extract was made by the percolation of 34 kilos. of dried leaves with cold wood spirit, concentrated to a few litres in a vacuum, and mixed with twice the volume of water. The *aqueous solution* yielded: (1) an ethereal extract containing 0·45 gram of a neutral *substance*, $C_{14}H_{18}O_4$, m. p. 133°; (2) a chloroform extract containing 55 grams of indefinite material; (3) a lead acetate precipitate, from which nearly 18 grams of a lemon-yellow *acid*, $C_{31}H_{32}O_{16}$, crystallising from pyridine in plates with 1·5 mols. of solvent, and forming a *deca-acetate*, m. p. 191—192°, was recovered; *d*-glucosazone, corresponding with 1·2% of lævulose in the drug; a phosphotungstic acid precipitate, from which choline equivalent to 0·025% of the drug was recovered (this also contained the principal toxic substance, although efforts to isolate it were not successful), and 2·4% of adonitol, which is the pentitol corresponding with ribose. The *resin* yielded phytosterolin, pentriacontane, myricyl alcohol, phytosterol mixed with a lower homologue, and linolic and palmitic acids.   J. C. W.

Transformations of Inulin in the Tuber of the Jerusalem Artichoke during its Period of Rest. H. COLIN (*Compt. rend.*, 1918, **166**, 305—307).—During the winter months, the inulin is gradually converted into sucrose and levulosans, which have a lower specific rotation than inulin and are hydrolysed by invertase, and consequently are fermented by yeast.   W. G.

General and Physical Chemistry.

Drude's Theory of Dispersion from the Point of View of Bohr's Model and the Constitution of H_2, O_2, and N_2. A. SOMMERFELD (*Ann. Physik*, 1917, [iv], **53**, 497—550).—A theoretical paper in which the author discusses the question of the dispersion and magnetic rotation of gases on the assumption that the structure of the molecules is in accordance with Bohr's hypotheses. The theoretical considerations are applied to hydrogen, oxygen, and nitrogen, for which certain structures are assumed, and the calculated refractive, dispersive, and magnetic rotatory powers are compared with those found by experiment.　　　　H. M. D.

The Spectra of Isotopes and the Vibration of Electrons in the Atom. WILLIAM D. HARKINS and LESTER ARONBERG (*Proc. Nat. Acad. Sci.*, 1917, **3**, 710—714).—The wave-length of the line λ4058 in the spectra of ordinary lead and of lead from radium (radium-G) has been measured with great accuracy by the use of a 10-in. plane grating, giving a sixth order spectrum with a dispersion of 0·359 Å. per mm. The atomic weight of the specimen of radium-G employed had been found by Richards to be 206·34, compared with 207·18 for ordinary lead.

In order to avoid mechanical shifts, the two spectra were photographed simultaneously, the vacuum arc lamps employed as sources of light being interchanged from time to time during the taking of the records. In all, seventeen experiments were made, and the plates show in all cases that the wave-length of the line λ4058 in the spectrum of radium-G is greater than it is in ordinary lead, the average difference being equal to 0·0043 Å

The observations are said to establish definitely the existence of a measurable difference between the wave-lengths of corresponding lines in the spectra of isotopes. The photographs indicate clearly that the shift is real and cannot be explained by broadening.
　　　　　　　　　　　　　　　　　　　　H. M. D.

Arc Spectrum of Gadolinium. JOSEF MARIA EDER. (A communication from *Photochem. Lab. d. K. K. Graph. Lehr-u. Versuchsanstalt Wien*, 1467—1535; from *Chem. Zentr.*, 1917, ii, 362).—The author has investigated this spectrum with the aid of gadolinium products obtained by Auer by a fractionation which separated gadolinium from samarium and europium. The chloride gives a purer spectrum than the oxide. The tables of gadolinium lines measured occupy 62 quarto pages. The fractions containing europium prepared by Auer give indications spectroscopically of the presence of an unknown element lying between europium and samarium.　　　　　　　　　　　　　　　R. V. S.

The Spectrum of Nickel. J. E. PAULSON (*Physikal. Zeitsch.* 1918, **19**, 13—15).—An examination of the wave-lengths of lines,

In cross references to abstracts *Ind.* will be used in place of *J. Soc. Chem. Ind.*, 1918, **37**.

in the arc spectrum of nickel has shown the existence of thirty-three groups of eight lines with constant differences between the corresponding wave-numbers. The lines in question are tabulated and the relative intensities are shown.   H. M. D.

The Ultimate Rays of Great Sensitiveness of Columbium and Zirconium. A. DE GRAMONT (*Compt. rend.*, 1918, **166**, 365—368).—Under the conditions previously described for titanium (compare this vol., ii, 49), the ultimate rays of columbium which could be detected photographically were $\lambda = 4101\cdot0$, $4079\cdot7$, $4059\cdot0$. None of these was visible to the eye at dilutions much above 1 : 100. The ultimate rays of zirconium were $\lambda = 3496\cdot2$, $3438\cdot2$, $3392\cdot0$. The sensitiveness of the group of five rays in the blue, Zra, was small.   W. G.

Resonance Spectra of Iodine. R. W. WOOD (*Phil. Mag.*, 1918, [vi], **35**, 236—252. Compare A., 1913, ii, 994; 1914, ii, 233). —An account is given of further observations on the resonance spectra which are emitted by iodine vapour when this is excited by the light from a Cooper-Hewitt mercury lamp. An improved method of illumination is described.

The doublet series, which is excited by the green mercury line, has been found to extend towards the red end of the spectrum up to $\lambda 7685$. The photographs, obtained by means of plates sensitised with dicyanine, show most of the doublets of the series, the last doublet at $\lambda 7685$ being of the twenty-seventh order. It is probable that this represents the limit of the resonance spectrum, for the plates used were highly sensitive to beyond $\lambda 8500$. The position of the twenty-seventh order doublet is, moreover, approximately the same as the limit of the absorption spectrum.

If the plates are exposed to the resonance radiation for longer periods, the doublets are found to be accompanied by faint companion lines, some of which may be due to excitation by the satellites of the green mercury line, but the author considers that some are to be attributed to the stimulating influence of the green line itself. On greatly prolonged exposure, it is found that the doublets fuse together to form a series of wide bands. If a gas of the helium group is introduced into the iodine tube, the intensity of the doublets is greatly reduced, and a series of fluted bands makes its appearance. These bands, which occupy positions between the doublets, are not exhibited by the resonance spectrum of iodine in a vacuum. It is probable that the lines forming the doublets are themselves constituents of the fluted bands, and that the appearance of the bands in presence of an inert gas is due to a transfer of energy from one part of the vibrating system to another as a result of collisions between iodine molecules and molecules of the inert gas. It may in this way be possible to account for the complicated system of bands in the absorption spectrum, these bands being referred to simpler systems which can be excited separately.

If the iodine vapour in a vacuum is excited by means of a quartz mercury arc, complicated groups of lines are obtained in place of the doublet series. This is attributed to the circumstance that, under these conditions, the green mercury line has broadened to such an extent that it covers a number of the iodine absorption lines. The intensity distribution amongst the groups of lines produced by this multiplex excitation is approximately the same as the distribution in the doublet series. The complexity of the groups increases with the width of the green exciting line.

A short reference is made to the resonance spectra excited by the two yellow mercury lines, but these have not yet been examined in detail.
H. M. D.

Series Law of Resonance Spectra. R. W. Wood and M. Kimura (*Phil. Mag.*, 1918, [vi], **35**, 252—261. Compare preceding abstract).—The wave-lengths of lines in the resonance spectra of iodine are recorded and the law of distribution is discussed.

The series of strong doublets excited by the green line of the Cooper-Hewitt lamp has been examined with particular care, with the result that the frequency difference between the components is found to be constant and equal to 50. The spacing of the first member (shorter λ component) of each doublet is represented by the formula $1/\lambda_m = 183075 - 2131 \cdot 414 + 12 \cdot 734 m (m-1)/2$, in which λ_m is the wave-length of the first member of the doublet of the mth order. The agreement between the calculated and observed values is quite good up to the doublet of the fifteenth order, but as the order becomes greater the divergence increases.

Other series of doublets with constant frequency differences may be approximately represented by a similar formula.

The lines in the resonance spectrum excited by the yellow lines $\lambda 5769 \cdot 6$ and $\lambda 5790 \cdot 7$ have also been examined with reference to the law of distribution. The doublets in these groups of lines are not characterised by the same regularities as those in the groups excited by the green mercury line. The frequency difference between the components has not a constant value, but the spacing of the doublets in the groups of lines excited by the yellow line $\lambda 5769 \cdot 6$ is such that the difference between the successive values of $1/\lambda$ is nearly constant. The degree of constancy is not so pronounced for the case of the groups which are excited by $\lambda 5790 \cdot 7$.
H. M. D.

Absorption Spectrum of Oxyhæmoglobin in the Ultraviolet and Extreme Ultra-violet Regions. Toshikazu Mashimo (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 199—202).—Oxyhæmoglobin, purified by crystallisation, was dissolved in water and the photographic records obtained by interposing layers of this solution, varying in thickness in the ratio of the integral numbers from 1 to 42, between a carbon arc and the photographic plate, are compared. These records show an absorption band with the centre at $\lambda 350 \, \mu\mu$, which is possibly the same as that described by Peyrega

and Vlès as occurring at λ 333 $\mu\mu$ (*Compt. rend.*, 1912, **154**, 133). No absorption could be detected in the Schumann region.

H. M. D.

The Fluorescence of Cyano-compounds. HUGO KAUFFMANN (*Ber.*, 1917, **50**, 1614—1623).—See this vol., i, 113.

Rotation Inversion and Anomalous Rotation Dispersion. HERMANN GROSSMANN and MARIE WRESCHNER (*J. pr. Chem.*, 1917, [ii], **96**, 125—165).—The dextrorotatory power of tartaric acid in aqueous solution is probably due to the dissociation of the acid, because with increasing concentration of the solutions the rotation falls, and, indeed, the molten or solid acid is lævorotatory. Addition of acids such as hydrochloric or nitric acid to the aqueous solution depresses the dissociation, the normal rotatory dispersion curve which rises from red to violet becoming gradually altered by an increasing proportion of added acid until a falling curve results; during the inversion of the nature of the curve the latter exhibits a maximum, which gradually moves in the direction of increased wave-length as the concentration of added acid is raised. Acetic acid exerts a similar effect to hydrochloric and nitric acids, but is less powerful. Sulphuric acid at low concentrations gives an effect resembling that of nitric and hydrochloric acids, but at higher concentrations the curve again begins to rise, and, in pure sulphuric acid, tartaric acid shows rotation values $[\alpha]$ red $+69$ and $[\alpha]$ violet $+158·8$, which are above those observed with any other solvent. With boric acid the rotatory dispersion curve of tartaric acid is unaffected in type, probably because of the formation of complex compounds of the two acids (compare Grossmann and Wieneke, A., 1906, ii, 209).

On adding increasing quantities of sodium hydroxide to the dextrorotatory aqueous solution of sodium tartrate, the rising rotatory-dispersion curve gradually flattens, and then, after becoming coincident with the horizontal axis corresponding with zero rotation, finally falls below on to the negative side of this axis; this alteration is attributed to the reversible formation of a lævorotatory tetrabasic salt of the acid. The addition of a calcium, strontium, magnesium, or cerium salt to the solution of tartaric acid containing excess of sodium hydroxide causes the curve for the alkaline solution to alter its character and to become wholly positive, doubtless due to the formation of complex compounds; a zinc salt gives no such evidence of complex formation.

Malic acid in the pure condition is dextrorotatory, but in the ionised condition exhibits a lævorotation; the addition of acids to the aqueous solution, as with tartaric acid, tends to repress dissociation, and the rotatory dispersion curve for the solution, which normally falls as it passes from red to violet, rapidly changes into a rising positive curve with the addition of increasing quantities of acid. Again, sulphuric acid at low concentration behaves like the other aqueous mineral acids, but in pure sulphuric acid malic acid attains the extreme negative values $[\alpha]$ red $-27°$, $[\alpha]$ violet $-60·4°$,

The effect of excessive sodium hydroxide on the activity of sodium malate solution resembles that with aqueous sodium tartrate; the rotatory dispersion curve becomes gradually flattened, and finally passes over to the other side of the horizontal axis representing zero-activity, the transition in this case being upwards from the negative side to the positive.

So-called anomalous rotatory dispersion as evidenced by maximum and minimum values or by achromatism occurs only in the neighbourhood of zero rotation, and the evidence indicates that it is due to the presence of two optically active components of different optical activity. Lowry's suggestion (A., 1914, ii, 786), to use the terms "simple" and "complex" rotatory dispersion in place of "normal" and "anomalous," is commended. D. F. T.

The Relation of Position Isomerism to Optical Activity. XI. The Menthyl Alkyl Esters of Terephthalic Acid and its Nitro-derivatives. JULIUS BEREND COHEN and HANNAH SMITH DE PENNINGTON (T., 1918, **113**, 57—66. Compare A., 1916, ii, 206).—The average molecular rotation of seven menthyl alkyl esters of terephthalic acid is found to be $[M]_D^{20} -254°$, and the rotation of menthyl hydrogen terephthalate to be $[M]_D^{15} -259\cdot2°$, which may be compared with $-239°$ for menthyl benzoate, $-243°$ for menthyl alkyl phthalates, and $-332°$ for menthyl hydrogen phthalate. It appears, therefore, that the carbalkoxyl or carboxyl group has little influence, in the para-position, on the activity of the asymmetric carbon atom. In the case of some menthyl alkyl nitroterephthalates, it is likewise found that enhanced rotation is exhibited by those esters in which the nitro-group is adjacent to the active group. A strange abnormality is met with among these particular o-nitro-esters; the solutions in benzene have considerably higher rotations than the fused esters.

For details of the preparation and constants of these esters, see the original. J. C. W.

Absorption of Hard Röntgen Rays in Gases. MINNA LANG (*Ann. Physik*, 1917, [iv], **53**, 279—319).—The experiments described were made with highly penetrating rays, the absorptive powers of oxygen, nitrogen, air, carbon dioxide, hydrogen, sulphur dioxide, and methyl chloride being compared. The results obtained show the relative values of the absorption-coefficients for rays of varying penetrating power and the dependence of the absorptive power on the pressure of the gas. A comparison is made of the absorptive capacity of air for Röntgen rays and γ-rays. H. M. D.

Interpretation of Röntgen Spectra. L. VEGARD (*Ber. Deut. physikal. Ges.*, 1917, **19**, 328—343).—A theoretical paper, in which the author discusses the origin of the several series of lines which have been recognised in the high frequency spectra. It is assumed that the atoms are built up in accordance with Bohr's theory, and that the high frequency emission is to be explained on the lines adopted by this author.

According to Debye (A., 1917, ii, 434), the emission of the K series of lines is due to an inner ring of three electrons. This appears to be the most probable cause of the appearance of these lines, but it is shown that changes in a four-ring system of electrons may also account for the series.

The L and M series require the assumption of rings of electrons, the disturbance of which is associated with two or more energy quanta, and it is suggested that the origin of the L series is a seven-membered ring of electrons corresponding with two energy quanta, the l series an eight-membered ring with two quanta, and that the M series is due to a ring of nine electrons associated with three energy quanta.   H. M. D.

Atomic Structure on the Basis of Röntgen Spectra. L. VEGARD (*Ber. Deut. physikal. Ges.*, 1917, **19**, 344—353).—The theoretical considerations advanced in explanation of the origin of the K, L, l, and M series of high frequency lines (compare previous abstract) have led the author to devise models for the structure of the known elements. It is claimed that this system of models is in agreement with the periodicity in the properties of the elements. With increasing atomic number there is a gradual increase in the number of concentric electron rings, but each ring appears to retain its individual characteristics throughout the entire series of elements. Such characteristics are the number of the constituent electrons and the energy quanta with which these are associated. The number of quanta increases, in general, with the diameter of the ring.   H. M. D.

Resonance and Ionisation Potentials for Electrons in Cadmium, Zinc, and Potassium Vapours. JOHN T. TATE and PAUL D. FOOTE (*Proc. Nat. Acad. Sci.*, 1918, **4**, 9).—According to the observations of Franck and Hertz, there are certain definite potentials at which electrons cause the emission of rays by the atoms of a gas or vapour. Two types of collision occur, one of which is accompanied by the emission of a single frequency, whilst the other causes ionisation and gives rise to a composite spectrum. The corresponding potentials are distinguished as resonance and ionisation potentials, and these critical values of the potential have been determined for cadmium, zinc, and potassium vapours.

Within the limits of experimental error, the observed critical potentials agree with the values calculated from the quantum relation $hv = eV$, in which v is the frequency of the single line in the case of the resonance radiation and the limiting frequency of the line series when the radiation is due to ionisation.   H. M. D.

Nomenclature of the Radio-elements. ST. MEYER and E. VON SCHWEIDLER (*Zeitsch. Elektrochem.*, 1918, **24**, 36—38; *Physikal. Zeitsch.*, 1918, **19**, 30—32).—The authors, in a work published on radioactivity, have made a number of changes in the symbolic representation of radioactive substances. The changes, which have been assented to by twenty-nine German and Austrian chemists and physicists, consist chiefly in the following: (1) Isotopes are desig-

nated by Roman indices, for example, U_I, U_{II}. (2) Successive dis-integration products are designated by Arabic indices, for example, UX_1, UX_2. (3) Branched products are designated by dashes, for example, RaC', RaC'', the single dash indicating that the sub-stances are like polonium and the double dash those like thallium.

J. F. S.

The Colloidal State of Radioactive Substances. HILARY ZACHS (*Kolloid Zeitsch.*, 1917, **21**, 165—176).—Many recorded observations show that certain radioactive substances in neutral or slightly alkaline solution exhibit properties which are usually regarded as characteristic of colloids, although the concentration of the solution is very much smaller than that corresponding with saturation with respect to the hydroxide. It has been suggested that the behaviour of these radioactive solutions is due to the presence of colloidal impurities in the solution, but certain facts cannot be reconciled with this hypothesis.

In the attempt to obtain further information on the subject, the author has investigated the properties of radium-A, radium-B, and radium-C in various solvents, including water, ethyl alcohol, ethyl ether, ethyl malonate, and benzene. The nature of the solvent is of considerable influence on the behaviour of the solutions in an electric field. In the case of water solutions, for instance, radium-A is deposited on the anode, radium-B on the cathode, and radium-C to a small extent on the anode, whereas in alcoholic solution, radium-A is deposited on the cathode and radium-B and -C on the anode. The sign of the change of the colloidal particles does not depend entirely on the nature of the solvent, for in every case, particles of opposite sign appear to be present. The results obtained with alcoholic solutions show, moreover, that the relative amounts of substance deposited on the two electrodes vary with the applied potential. This effect has been previously noted in the case of colloidal solutions of silver.

The adsorption of the radioactive colloids by various adsorbents is also found to exhibit a similar variation when the solvent is changed. The variability is said to afford evidence of the presence of particles of different degrees of dispersity, and it is suggested that the radioactive substances occur in the form of ions as well as in colloidal form.

Although cellulose has but little adsorptive capacity for the radioactive substances, it is found that comparatively large quantities of the radioactive products remain on the filter when the above solutions are passed through an ordinary filter paper. This would seem to show that a considerable proportion of the radioactive dispersoid particles are of large dimensions, and the suggestion is made that these particles contain a very large number of solvent molecules.

The decay of radium emanation in a gas or vapour leads apparently to the formation of gaseous ions by the combination of the particles of radium-A, -B, and -C with the molecules of the gas or

vapour present. This type of combination or condensation seems to be very different in kind, however, from that which occurs in liquid solvents, in which, apparently, the degree of solvatation is such that colloidal properties are developed.   H. M. D.

Radioactive Minerals in Bavaria. II. F. HENRICH (*J. pr. Chem.*, 1917, [ii], **96**, 73—85).—The view that the fluorspar (so-called "Stinkfluss") of Wölsenberg, near Wölsendorf, in the Upper Palatinate, owes its colour and odour to radioactive influences has been experimentally tested.

Crystallised colourless fluorspar can be coloured deep blue by the β- and γ-rays of radium, and then shows on gentle warming a beautiful green thermoluminescence, which fades and changes into the pale violet light characteristic of all fluorspars. But neither by radium nor by positive rays (Kanalstrahlen) could the characteristic odour of Wölsenberg fluorspar be produced. According to O. Ruff, this odour, which is produced when the mineral is crushed, is typical of free fluorine, and indeed the mineral may be used to demonstrate conveniently the odour of this difficultly prepared element.

The second part of the paper deals with the detailed analysis of copper–uranium mica (chalcolite or tobernite) from Steinbruch Fuchsbau, near Leopoldsdorf, in the Fichtelgebirge, the composition of which agreed closely with the formula

$$Cu(UO_2)_2(PO_4)_2,11\cdot5H_2O.$$
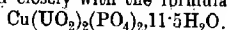
F. S.

The Radioactivity of Archæan Rocks from the Mysore State, South India. W. F. SMEETH and H. E. WATSON (*Phil. Mag.*, 1918, [vi], **35**, 206—214).—Some fifty radium estimations have been made of representative samples from the various components of the Archæan complex of Mysore, in order to see how far the various formations or groups are distinguishable by their radioactivity. These are set forth in order of age of the rock in a table. The oldest, the hornblende rocks (epidiorites and hornblende schists) of the Dharwar system, are low in radium and uniform, between 0·14 and 0·25 ($\times 10^{-12}$ gram of radium per gram of rock), and the rocks of the chloritic series, next in age, do not differ much from them. Intrusions of the Champion gneiss and the related quartz veins of the Kolar Field, which contain much more radium than the normal schists, considerably increase the radium content, whereas the basic intrusions of Dharwar age contain much less radium than the schists themselves. On radioactive evidence, the original classification which correlated the Bellara trap with the Grey trap of Chitaldrug is correct, rather than the newer correlation of the latter with the Santaveri trap of the Kadur district, which resembles it closely, but contains three times as much radium as the other two. This affords an example of the possible use of such determinations in the correlation of the highly metamorphosed members of the Archæan complex.

The Champion gneiss, Peninsular gneiss, and Closepet granite, next in age, contain four to five times as much radium as the Dharwar schists and twelve to fifteen times as much as the next and following Charnockites, which stand apart from the others in virtue of exceedingly low radium content. This confirms Holland's classification of Charnockites as a distinct petrographical province.

The general conclusions are that these very ancient rocks, all supposed to be of igneous origin, contain remarkably little radium. For the fairly uniform hornblendic schists of the Kolar Field, the radium content does not vary with the depth from the surface. Amongst magmas, the more basic contain less radium than the more acid, the Charnockite magma of intermediate composition being a striking exception.   F. S.

Influence of Heat Treatment on the Electrical and Thermal Resistivity and Thermo-electric Potential of some Steels.

EDWARD D. CAMPBELL and WILLIAM C. DOWD (*J. Iron Steel Inst.*, 1917, **96**, 251—266).—In a series of annealed and hardened steels containing from 0·018 to 1·184% of carbon, the ratio of the electrical resistivity to the relative thermal resistivity is in all cases higher than for pure iron. The effect of quenching is to raise both values. The thermo-electric potential varies with the nature as well as with the concentration of the elements dissolved in the iron. [See, further, *Ind.*, 1917, 1051.]   C. H. D.

A Permanganate Electric Cell.

A. W. WARRINGTON (*Chem. News*, 1918, **117**, 97—98).—Potassium permanganate is used as the depolarising agent in a two-fluid electric cell, in which the carbon plate is immersed in a dilute solution containing 3·16 grams of potassium permanganate and 6 c.c. of concentrated sulphuric acid in 250 c.c. of liquid, contained in a porous pot. The outer zinc compartment, of 750 c.c. capacity, contains a strong solution of zinc sulphate (14·55 grams). The cell gave a voltage of about 2. Two such cells were connected up to a water voltameter and tangent galvanometer in series, and, after the first ten minutes, the fall in current in a run extending over three hours forty-six minutes was from 0·09 to 0·085 ampere only, and the voltage at the end was still 3·7. With a single-fluid permanganate cell containing the same amounts of permanganate and sulphuric acid with amalgamated zinc and carbon, the current, after ten minutes, fell from 0·0538 to 0·0358 ampere in 146 minutes, whilst the voltage at the end was 1·5. The yield of current with very dilute solutions in a two-fluid cell is very high, and a cell containing 0·79 gram of potassium permanganate and 2·64 grams of sulphuric acid in 250 c.c. of liquid, and 3·59 grams of crystallised zinc sulphate in 750 c.c., deposited 0·48 gram of copper in three hours, whilst nearly 75% of the energy was still available. A similar dichromate cell, containing 5·88 grams of potassium dichromate and 13·72 grams of concentrated sulphuric acid in the carbon compartment, gave an average current of 0·0632 ampere only.   B. N.

The Magnetic Properties of Manganese and of some Manganese Steels. SIR ROBERT HADFIELD, C. CHÉNEVEAU, and CH. GÉNEAU (*Proc. Roy. Soc.*, 1917, [*A*], **94**, 65—87; *Compt. rend.*, 1918, **166**, 390—392).—Measurements have been made of the coefficient of magnetisation of manganese, free from occluded gases, and a number of manganese steels. Manganese is paramagnetic. [For numerical data, see *Ind.*, 12A.]   W. G.

Energy Theory of Matter. ELMER B. VLIET (*Chem. News*, 1918, **117**, 118—119).—It has been pointed out by Thornton (A., 1917, ii, 164) that the molecular heat of combustion of an organic compound is proportional to the number of oxygen atoms which is required for the complete combustion of one molecule of the organic substance. According to Redgrove (A., 1917, ii, 411), the molecular heat of combustion can be represented by an additive series of terms which depend on the number and type of the valency bonds in the molecule.

By applying these relations to the aliphatic hydrocarbons, it is shown that the coefficients characteristic of the several terms in Redgrove's series may be calculated. The values so obtained differ from those calculated by Redgrove, and the conclusion is drawn that the molecular heat of combustion cannot be regarded primarily as a function of the number and type of the valency bonds. It is, however, still possible that the energy change accompanying a reaction may depend on the valency changes.

H. M. D.

A High Temperature Thermostat. J. L. HAUGHTON and D. HANSON (*J. Inst. Metals*, 1917, **18**, 173—186).—The instrument consists in principle of a double-walled vessel, like a Bunsen ice calorimeter, made into a furnace by winding with nichrome wire. The vessel acts as a gas thermometer, and the variations of pressure of the air contained in it operate a contact-breaker, consisting of a U-tube containing mercury with two platinum contacts, through which passes a relatively small current. The latter, by means of a solenoid, pulls a fork out of or into two mercury cups, so introducing an external resistance into the heating circuit or cutting it out. The other side of the U-tube is connected with a second thermostat of simpler construction, which serves to compensate for changes of external pressure and temperature.

The furnace bulb is made of silica, and may be used for temperatures of the order of 1000°. The U-tube has a tap for removing the mercury when fouled by sparking, and is made sufficiently wide in the upper part of the limbs to prevent the mercury from being sucked back when the furnace is shut off. The cold thermostat consists of three concentric cylinders, of which the inner one acts as the air-bulb, and is surrounded by benzene contained in the middle vessel, on which a fine resistance wire is wound. The benzene, in expanding, operates a mercury contact-breaker. The third cylinder contains insulating material. With this arrange-

ment, the temperature of this part of the apparatus is constant within less than 0·1°. The main furnace is then kept constant within 1°.

By connecting another furnace, such as a crucible furnace, in series with the main regulating resistance, but in parallel with a thermostat furnace, the temperature of the former may be kept constant with about the same accuracy as the thermostat. By automatically reducing a resistance in parallel with the controlled furnace, very regular cooling may be obtained, such as is required in taking cooling curves. C. H. D.

Adsorption Compounds and Adsorption. III. The Influence of the Adsorption of certain Substances by Alcohol. L. BERCZELLER and ST. HETÉNYI (*Biochem. Zeitsch.*, 1917, **84**, 137—148).—A number of measurements are given of the adsorption of alkali hydroxides, acetic acid, iodine, methylene-blue, etc., by starch, charcoal, etc., and the influence of the additions of alcohols. The influences of isocapillary and equimolecular solutions of the alcohols on adsorption were compared. Generally, the isocapillary solutions did not exert the same amount of inhibition, the solutions of lower alcohols, which contain a relatively large amount of alcohol, exerting a greater inhibition than isocapillary solutions of the higher alcohols. Those isomolecular solutions of which the surface tensions are lowest exert, however, a greater inhibitory action. S. B. S.

Gliding Dialysis. II. H. THOMS (*Ber.*, 1918, **51**, 42—45. Compare A., 1917, ii, 561).—Instead of rotating the dialyser about the plane of the membrane, it may be rotated or shaken in the same plane, with equally good results. The new arrangement is an improvement, inasmuch as it imposes very little tearing strain on the membrane. [See, further, *Ind.*, 190A.] J. C. W.

Solubility and Dissociation of some Electrolytes in Ethylurethane. M. STUCKGOLD (*J. Chim. Phys.*, 1917, **15**, 502—516).—The author has determined the solubilities of the following salts in ethylurethane at 60°: ammonium, rubidium, potassium, tetramethylammonium and tetraethylammonium iodides, sodium, potassium, rubidium, and tetramethylammonium bromides, sodium, potassium, and ammonium chlorides. The conductivities of six electrolytes, namely, ammonium, potassium, and tetraethylammonium iodides, tetramethylammonium bromide, cobalt nitrate, and zinc nitrate, have been determined, those of the iodides being taken to the greatest dilutions suitable, considering experimental errors. The cryoscopic constant of this solvent, using naphthalene, carbamide, and nitrotoluene as solutes, was found to be 53·2, and from this, molecular weight determinations by the cryoscopic method indicated that ammonium, potassium, and rubidium iodides are dissociated in ethyl urethane.

Molecular weight determinations on ethylurethane, based on the

7*—2

capillarity constant, using the formula $M = 0.6T(4.8 - \log p)/a_2$, where T is the absolute b. p. at p mm. of mercury and $a_2 = h \cdot r$, where h is the height of ascension and r the radius of the capillary in millimetres, show that ethylurethane is strongly polymerised, the factor of association being almost independent of the temperature over the range 65—179°. The viscosities and densities of the urethane at 60°, 70°, and 80° were also determined.   W. G.

Ultrafiltration of Supersaturated Solutions. L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 156—159).—Supersaturated solutions of menthol, thymol, and naphthol were filtered through collodion membranes, and the surface tensions of filtrate and residue were determined by the stalagmometer. In certain cases, the results (lower surface tension of residue) indicated that some of the solute was retained on the filter, from which fact the conclusion is drawn that the supersaturated solution is colloidal in character.

S. B. S.

Colloidal Nature of the γ-Alkali Resin Soaps. LUDWIG PAUL (*Kolloid Zeitsch.*, 1917, **21**, 176—191).—A general account is given of the properties of solutions of sodium and ammonia resin soaps in which particular attention is directed to the colloidal properties of the solutions and to differences between the resin and fatty acid soaps. Dilute solutions of the alkali resin soaps represent highly disperse colloid systems of very pronounced stability. On the addition of basic dyes, such as methyl-violet and magenta, colloidal lakes are formed which can be kept without change for prolonged periods of time. The lakes are coagulated on the addition of suitable electrolytes.

On addition of hydrochloric acid to the γ-alkali resin soaps, γ-pinic acid is obtained, and this behaves very similarly to the soaps towards basic dyes. [See *Ind.*, April.]   H. M. D.

Colour and Degree of Dispersity [of Colloidal Solutions]. L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 156—174).—Gold sols have varying colours, according to the size of the colloidal particles, and Harrison (A., 1912, ii, 240) has directed attention to the similarity of the colours of the adsorption complexes of iodine with starch and dextrins, where similar variations of colour are produced by varying the size of the particles of the carbohydrate. The author shows that similar variations in the colour of the adsorption complexes of lanthanum hydroxide can be produced by varying the size of the particles of the hydroxide. Attention is also directed to analogies in the colour variations in certain complex copper compounds, in certain reactions of bile pigments, in some furfuraldehyde reactions (Udránszky, A., 1889, 1024; 1891, 350), and in the nuances of solutions of dyes when subjected to varying treatments (heating, dilution, treatment with salts, etc.).

S. B. S.

Anisotropic Colloidal Solutions. W. REINDERS (*Kolloid Zeitsch.*, 1917, **21**, 161—165. Compare Diesselhorst and Freundlich, A., 1916, ii, 65; Kruyt, *ibid.*, ii, 486).—With a view to the explanation of the double refraction which is exhibited by certain colloidal solutions, further experiments have been made with vanadium pentoxide sols which seem to show that the particles of such sols are crystalline. By varying the conditions of formation of the pentoxide, it has been found that there is no clear line of demarcation between the particles which are present in the initially isotropic sols and those which can be microscopically identified as crystalline particles. Although the double refracting power of a sol is only developed very slowly at the ordinary temperature, the transformation takes place much more quickly at 100°. In the freshly prepared sols, the ultra-microns are spherical, but on heating at 100°, elongated ultra-microns make their appearance in a short time. These increase in size and number, and the change is accompanied by a considerable increase in the viscosity.

Experiments made with mercurous chloride and lead iodide gave similar results. If these substances are prepared by double decomposition in presence of a protective colloid, doubly refracting sols are obtained, but there is a continuous transition from the sol condition to that which is represented by crystalline suspensions of these substances.

The anisotropic character of the sols in question appears therefore to be due to the crystalline nature of the ultra-microns.

H. M. D.

Kinetics of the Reactions in the Formation and Flocculation of Colloidal Solutions. L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 175—182).—Iodic acid accelerates the reduction of gold chloride solutions by sulphurous acid, as do also mercuric salts, and the colour of the sols varies in the latter case with the salt used. Examples are given of the influence of capillary active substances (hexoic and decoic acids) on the flocculation of colloidal gold and starch solutions, which are cases of sensitisation of colloids to salt precipitation, as recently demonstrated by Freundlich and Rona (A., 1917, ii, 365). S. B. S.

Coagulation and the Attraction of Particles. RICHARD ZSIGMONDY (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 1—43; from *Chem. Zentr.*, 1917, ii, 350—351 *).—The paper deals with the possibility of determining the attraction (if any) between discharged colloidal particles from measurements of the rate of coagulation. Experiments in which the changes of colour of gold hydrosols were employed as an indicator of the progress of the coagulation showed that a pure colloidal gold solution of a given nature and concentration has a certain minimum time of coagulation, independent of the nature, and to a great extent independent of the concentration, of the electrolyte employed. The period of rapid coagulation is reached before the particles are completely discharged, but the

* and *Zeitsch. physikal. Chem.*, 1918, **92**, 600—630.

remaining charges are small (compare Hardy and Powis, *Zeitsch. physikal. Chem.*, 1915, **89**, 179). The time of coagulation is approximately proportional to the gold concentration. A method of observing the progress of coagulation ultramicroscopically is given, and by this means the diminution in the number of primary particles and the production of secondary particles (which shine more brightly) were determined. From these results, it is calculated that the sphere of attraction of a primary particle is two or three times its radius. This is in agreement with the results obtained by other writers in other ways. It is proved, therefore, that the discharged particles do attract one another when they come within this distance of each other.   R. V. S.

Retardation of the Formation of Prussian Blue and other Reactions in Aluminium Hydroxide Sols. JOSEF REITSTÖTTER (*Kolloid Zeitsch.*, 1917, **21**, 197—200).—In the course of observations on the coagulation of aluminium hydroxide sols in presence of various alkali metal salts (Gann, A., 1916, ii, 382), it was found that after coagulation by the addition of a very dilute solution of potassium ferrocyanide, the solution gave no blue coloration on the addition of ferric ions until after the lapse of a considerable interval of time. To explain this effect, it was suggested that the ferrocyanide ions are adsorbed and subsequently enveloped by the coagulate.

Further experiments show that the retardation is very much less pronounced if some other coagulating electrolyte, such as sodium citrate, is added to the sol either before or after the addition of the ferrocyanide. In these circumstances, it is more probable that the retardation of the formation of Prussian blue is to be explained by the adsorption of both the ferrocyanide and the ferric ions. If either or both are then displaced by other ions, conditions favourable to the formation of Prussian blue are obtained.

Similar retardation phenomena have been found when a little of the blue sol obtained by acidifying Congo-red is mixed with a colloidal solution of aluminium hydroxide and a drop of sodium hydrogen carbonate solution is added to the mixture. The blue sol may be replaced by benzopurpurin or rosolic acid. [See *Ind.*, 71A.]   H. M. D.

General Curves for the Velocity of Complete Homogeneous Reactions between Two Substances at Constant Volume. GEORGE W. TODD (*Phil. Mag.*, 1918, [vi], **35**, 281—286). —By choosing suitable quantities to represent the concentration of the reacting substances, it is possible to plot curves showing the connexion between the rate of change and the time, which are applicable to all reactions of the same type. The mode of representation may be illustrated by reference to the bimolecular velocity equation $dx/dt = k(a-x)(b-x)$. If $X = x/a$, $K = ka$, and $p = b/a$, this equation assumes the form $dX/dt = K(1-X)(p-X)$, and on integration this gives $Kt = 1/(1-p) \cdot \{\log p(1-X)/(p-X)\}$. The curves referred to are then obtained by plotting X against Kt for values of $p = 1{\cdot}5$, 2, 3, etc.

Corresponding series of curves are plotted for the termolecular reaction represented by $2A + B \longrightarrow$ for the three cases in which the initial concentration of A is equal to, greater, and less than that of B. Curves for the quadrimolecular reaction $3A + B \longrightarrow$ and $2A + 2B \longrightarrow$ are also shown.

These general curves may be applied in practice for the determination of k, of the value of X corresponding with a given time interval, or for the determination of the order of a reaction. If the order of the reaction and the initial concentration are known, it is only necessary to measure X corresponding with a certain value of t, and the curves then give Kt, and therefore k. The fraction X changed in a given time may be read off from the curves if the order of the reaction, the coefficient k, and the initial concentrations are known. To find the order of a reaction, it is necessary to know the initial concentrations and two corresponding values of X and t. The particular curve on which the two points (X, t) fit most exactly determines the order of the reaction.

H. M. D.

Relationship between the Saponification Velocity Constants of Esters. P. E. VERKADE (*Chem. Weekblad.*, 1918, **15**, 203—208).—The author finds that the ratio of the velocities of saponification of mixed anhydrides of acetic, propionic, etc., acids with different acids is always the same. A. J. W.

Velocity of Saponification of certain Esters by Tenth-normal Potassium Hydroxide in Different Solvents at 25°. ERNEST ANDERSON and H. B. PIERCE (*J. Physical Chem.*, 1918, **22**, 44—67).—The object of these experiments was to determine whether the relative velocities of saponification of different esters are affected by the nature of the solvent and whether the relative rates of saponification of different esters containing the same alcohol (or acid) are independent of the nature of the alcohol (or acid).

The rates of saponification of twenty-three esters were measured at 25° in 90% methyl alcohol, 90% ethyl alcohol, *iso*amyl alcohol, D_{15}^{25} 0·8166, and, when possible, in water. The results obtained show that the relative values of the velocity coefficients in the different solvents vary considerably with the nature of the ester. Esters containing the same alcohol (acid) are saponified at relative rates which depend on the nature of the alcohol (acid).

H. M. D.

Hydrolysis of Triethyl Citrate and the Ethyl Hydrogen Citrates. JOH. PINNOW (*Zeitsch. Elektrochem.*, 1918, **24**, 21—36). —The hydrolysis of triethyl citrate, symmetrical and unsymmetrical diethyl hydrogen citrate, and symmetrical and unsymmetrical ethyl dihydrogen citrate by means of sodium hydroxide has been studied at a series of temperatures from 0° to 100°. The hydrolysis of the various stages is shown to take place at very different velocities between the temperatures of 8° and 50°. Each step in the hydrolysis may be separated from the others, and goes to completion as

a strictly bimolecular reaction. The side ethyl groups are the first to be removed, and in no circumstances do symmetrical diethyl hydrogen citrate or unsymmetrical ethyl dihydrogen citrate appear in recognisable quantities as products of any of the hydrolyses. These products are only obtainable by the esterification of citric acid. The preparative separation of the mono- and di-ethyl esters from one another and from citric acid can be effected by ether extraction from aqueous solution in a Partheil-Rose apparatus. The various esters were identified by measurements of their hydrogen ion concentration by means of the colorimetric process of Friedenthal, Salesky, and Salm. The temperature coefficient of the rate of hydrolysis is high for all five compounds at temperatures below 23°; in the case of the unsymmetrical diethyl ester and the monoethyl esters a minimum is shown between 23° and 30°, and a second minimum for the monoethyl esters between 45° and 60° and 38° and 45° respectively. The stepwise hydrolysis and the first minimum of the temperature coefficient are explained by the formation of additive products between the ester and the alkali, these compounds undergoing decomposition as the hydrolysis proceeds into the original compounds. The following reaction constants and temperature coefficients have been found: Hydrolysis of triethyl citrate, $k = 37.8$ at $8.1°$, 63.7 at $15°$, 98.9 at $23°$, 149.8 at $30°$, 253 at $40°$, and 443 at $50°$; increase of $\log k$ for $10°$ between the successive temperatures is 0.328, 0.239, 0.259, 0.227, and 0.243. Unsymmetrical diethyl hydrogen citrate, $k = 1.725$ at $8.1°$, 2.92 at $15°$, 4.28 at $23°$, 5.14 at $30°$, 9.38 at $40°$, 16.17 at $49°$; increase of $\log k$, 0.330, 0.208, 0.114, 0.262, and 0.263. Symmetrical diethyl hydrogen citrate, $k = 0.474$ at $6.7°$, 0.841 at $15°$, 1.48 at $23°$, 2.27 at $30°$, 4.16 at $40°$, and 6.84 at $50°$; increase of $\log k$, 0.300, 0.306, 0.266, 0.263, and 0.216. Symmetrical monoethyl hydrogen citrate, $k = 0.0038$ at $0°$, 0.0149 at $15°$, 0.0283 at $23°$, 0.0409 at $30°$, 0.0743 at $38°$, 0.1153 at $45°$, 0.245 at $60°$, 0.584 at $75°$, and 2.86 at $100°$; increase of $\log k$, 0.395, 0.349, 0.229, 0.324, 0.273, 0.218, 0.251, and 0.276. Unsymmetrical monoethyl hydrogen citrate, $k = 0.0825$ at $8°$, 0.132 at $15°$, 0.238 at $23°$, 0.302 at $30°$, 0.511 at $38°$, 0.654 at $45°$, 0.080 at $55°$, 1.76 at $65°$, and 10.65 at $100°$; increase of $\log k$, 0.291, 0.320, 0.147, 0.285, 0.154, 0.217, 0.213, and 0.212. The figures in all cases refer to the hydrolysis of a single ethyl group.   J. F. S.

Rate of Solution of Silver in Chromic Acid.

R. G. VAN NAME and D. U. HILL (*Amer. J. Sci.*, 1918, [iv], **45**, 54—58).— The measurement of the rate at which silver dissolves in chromic acid solutions containing sulphuric acid has shown that the initial velocity is greater than the velocity which characterises the normal dissolution process. The anomaly indicates that the velocity depends on the physical state of the metal, and this in turn suggests that the rate of dissolution of the metal is not entirely determined by diffusion process.

Previous experiments have shown that the rates of dissolution of different metals tend to become more nearly equal as the concentra-

tion of the sulphuric acid in the solution increases. The behaviour of cadmium and silver forms an exception to this rule, in that the relative rates of dissolution diverge with increasing acid concentration. H. M. D.

Contact Catalysis. IV. WILDER D. BANCROFT (*J. Physical Chem.*, 1918, **22**, 22—43. Compare this vol., ii, 40).—A discussion of false equilibria in reference to the poisoning of catalysts by the adsorption of one or other of the products of reaction. Such adsorption will cause the reaction to slow down, and it may be brought practically to a standstill. In these circumstances, an apparent or false equilibrium is reached which will depend on the relative amount of the catalyst present. It is probable that molten sulphur catalyses the reaction between hydrogen and sulphur, and that hydrogen sulphide acts as a poison towards the catalyst. A similar effect is supposed to obtain in the reaction between hydrogen and selenium.

Enzyme reactions are in many cases affected by the products of reaction, in that a large quantity of enzyme is required to complete the reaction. In such cases, false equilibria are set up which may be explained in terms of the poisoning of the enzyme by one or other of the reaction products. H. M. D.

The Variations in the International Tables of Atomic Weights. TH. RENARD (*J. Chim. phys.*, 1917, **15**, 541—548).— A brief discussion of the revisions made of the various atomic weights by the International Committee since 1903. The author advocates the use of the rounded-off values suggested by Guye (compare A., 1916, ii, 386). W. G.

Hydrogen Isotopy. A. E. LACOMBLÉ (*Chem. Weekblad*, 1918, **15**, 38—40).—Polemical. A criticism of the views expressed by Scheringa (*ibid.*, 1917, **14**, 953) on the relationship of Prout's hypothesis to the periodic system. A. J. W.

Prout's Hypothesis and the Periodic System. K. SCHERINGA (*Chem. Weekblad*, 1918, **15**, 221).—A reply to Lacomblé (preceding abstract). A. J. W.

The Exchange of Energy in the Collisions between Slowly-moving Electrons and Molecules of Gases. G. HERTZ (*Ber. Deut. physikal. Ges.*, 1917, **19**, 268—288).—A theoretical paper in which the laws governing the exchange of energy between colliding electrons and molecules are discussed in reference to atomic and molecular structure. From the available data for helium, it is calculated that the loss of energy in the collision between an electron and a helium atom is 0.00027 times the energy of the electron. This result is very nearly the same as that which is derived on the assumption that the laws of collision are those governing collisions between elastic spheres, and from the close

agreement the conclusion is drawn that the energy lost by the electron is represented by the increase in the kinetic energy of the helium atom. In the case of hydrogen, however, the loss of energy is found to be much greater, namely, 0·06 of the energy of the electron, and it would seem that the collision of an electron with a hydrogen molecule is accompanied by an increase in the internal energy of the molecule.

The movement of electrons in gases at higher pressures and the influence of small quantities of impurities on the effects produced are also discussed from the point of view of the author's theory.

H. M. D.

Valency Centres. III. The Periodic System. O. Hins-berg (*J. pr. Chem.*, 1917, [ii], **96**, 166—173. Compare A., 1916, i, 725; 1917, ii, 173, 461).—As explained in the earlier papers, the atoms of the elements lithium, glucinum, boron, and carbon are assumed to possess one valency centre, the chemical valency of which ranges from one to four, the maximum being attained at carbon; in the remaining elements of the first group, the atoms contain two valency centres, one being quadrivalent throughout and the other gradually increasing in valency from 1 to 4, so that the surplus or normal valency falls in the order 3, 2, 1, 0 for nitrogen, oxygen, fluorine, and neon respectively. Similar differences exist in the second series of the periodic system; a single valency centre or atomic nucleus is present in the first four members, but at the fifth element, namely, phosphorus, a second valency centre enters, and the remainder of the elements of the series up to argon contain the two atomic nuclei which in the last element just satisfy one another and leave the element without free valency; contrary to the earlier opinion, chlorine probably contains only two valency centres, this view receiving support from the similarity in the general properties of the chlorides and cyanides, and the analogy between the intra-atomic structure of the chlorides and the intra-molecular structure of the cyanides, for example, $\overset{\frown}{\underset{\smile}{\cdots}}$–Ag for silver chloride and N–C–Ag for silver cyanide. In the next series, a different type is encountered; the assumption is made that in these elements a sexavalent atomic nucleus is present, in which the active valency increases by units from potassium up to the maximum of six, which is attained at chromium; the atoms of the succeeding elements, manganese, iron, cobalt, and nickel, include an additional valency centre which possesses an additional free valency at each element named, so that the maximum possible valency for these metals is 7, 8, 9, and 10 respectively, the maximum apparently being attained in iron carbonyl, $Fe(CO)_4$, with octavalent iron; in the case of cobalt, the full possible nonavalency is never reached, the differential valency, or the difference between the valency of the sexavalent and tervalent nuclei supplying the maximum; with nickel also the differential valency has a value 2, in agreement with the composition of most of the compounds,

although in nickel carbonyl, $Ni(CO)_4$, the atom appears to attain octavalency, but, however, is still short of decavalency. The metallic nature of the whole of the ten elements of this third series is ascribed to the presence of the sexavalent atomic nucleus. Copper is regarded as a transition element between the third and fourth series, and therefore probably abnormal; from zinc onwards, the members of the fourth series fall into a normal group, the valency of the first atomic nucleus gradually increasing in valency until quadrivalent germanium is reached; after this point, the atoms of this series contain a second atomic nucleus the valency of which gradually increases from unit value in arsenic to 4 in krypton, the latter therefore being devoid of free valency. For the present, the theory is extended only as far as the fifth and sixth groups; the elements of the former contain as their essential characteristic a sevavalent atomic nucleus which exerts its full effect in molybdenum, the last four elements of the group (one unknown) including an additional nucleus, but the final elements, namely, rhodium and palladium, exert only their differential valency. Silver, like copper, is probably an abnormal transition element. The sixth series, from cadmium to xenon, is normal, and corresponds with the zinc-krypton group.   D. F. T.

Inorganic Chemistry.

The Hydrides of the Metalloids. R. DE FORCRAND (*J. Chim. phys.*, 1917, **15**, 517—540).—An elaboration of work already published (compare A., 1905, ii, 696) and a discussion of Berthoud's work on this subject (compare A., 1917, ii, 237).   W. G.

Hydrogen Peroxide as a Reducing Agent. M. KLEINSTÜCK (*Ber.*, 1918, **51**, 108—111).—Silver chloride, suspended in potassium hydroxide solution, is quickly reduced by hydrogen peroxide according to the equation $2AgCl + H_2O_2 + 2KOH = 2Ag + O_2 + 2KCl + H_2O$.

Carbonyl chloride and phenyl carbonate also react with alkaline hydrogen peroxide, and so does a saturated solution of potassium hydrogen carbonate if kept at 100° in a pressure bottle. The distillate obtained by passing steam through the products reduces ammoniacal silver oxide, and is therefore said to contain formaldehyde. The author sees in these reactions a new interpretation of the assimilation of carbon dioxide by plants. thus: $H_2CO_3 + H_2O_2 = CH_2O + H_2O + 3O$. [See also *Ind.*, April.]   J. C. W.

Variations of the Density of Air and the Loomis-Morley Law. PH. A. GUYE (*J. Chim. phys.*, 1917, **15**, 561—566).—A study of the results obtained by various workers for the weight of a normal litre of air, in which it is shown that the results, taken as

a whole, verify the qualitative experimental relation, stated by Loomis and Morley, between the density of the air and the barometric pressure. The most probable explanation of such variations in density is based on the presence in the air of varying quantities of dust, invisible under the ultramicroscope. The mean of the most modern determinations gives the value $1 \cdot 2928$ grams as the weight of a normal litre of air.   W. G.

Portable Hydrogen Sulphide Generator.   W. FAITOUTE MUNN (*J. Ind. Eng. Chem.*, 1918, **10**, 130—131).—A wide glass tube has two bulbs formed at its lower end, the bottom bulb being provided with a draw-off tap. A perforated lead plate is fitted at the constriction between the bulbs (a piece of glass tubing in the lower bulb acts as a support for the plate) and ferrous sulphide is filled into the upper bulb. The acid reservoir consists of a large bulb, the stem of which passes through a cork closing the top of the wide glass tube and extends to the bottom of the lower bulb. A tapped exit tube for the gas is placed near the top of the wide tube, and this exit tube is fitted with a small washing tube.

                                                          W. P. S.

Automatic Hydrogen Sulphide Stopcock.   CARL H. CLASSEN (*J. Ind. Eng. Chem.*, 1918, **10**, 131—132).—To the delivery tube of the hydrogen sulphide apparatus is attached a length of rubber tubing in which is inserted a glass " pearl " made from glass tubing having a diameter slightly larger than that of the rubber tubing. When the rubber tubing over the " pearl " is compressed between the finger and thumb, a channel for the flow of the gas is formed between the glass and the rubber.   W. P. S.

Chloro- and Bromo-aminosulphonic Acids.   WILHELM TRAUBE and E. VON DRATHEN (*Ber.*, 1918, **51**, 111—115).—Solutions of potassium aminosulphonate and hypochlorous acid in equivalent proportions react in the cold to form *potassium chloroaminosulphonate*, $NHCl \cdot SO_3K$, which may be isolated by evaporating the mixture to a small bulk, in a high vacuum, at as low a temperature as possible and precipitating with alcohol. The salt forms limpid, hygroscopic crystals, and is comparatively stable. When warmed with mineral acids, hydrolysis takes place according to the equation $NHCl \cdot SO_3H + H_2O = NH_2Cl + H_2SO_4$. The corresponding *barium* salt is not so stable, but *potassium bromoaminosulphonate* is very similar.

Similar salts may be prepared by the interaction of free aminosulphonic acid and metallic hypochlorites. Alkylaminosulphonates apparently give very unstable products, for evolution of gas is noticed as soon as hypochlorous acid is added.

There are indications that a double amount of hypochlorous acid produces less stable dichloroaminosulphonates.   J. C. W.

Rate of Hydrolysis and Electrical Conductivity of Hypophosphoric Acid Solutions.   R. G. VAN NAME and WILBERT J. HUFF (*Amer. J. Sci.*, 1918, [iv], **45**, 103—118).—The iodometric

method for the estimation of phosphorous acid in presence of hypo-phosphoric acid (this vol., ii, 128) has enabled the authors to in-vestigate the rate of hydrolysis of the latter acid. The data obtained at 25° and 60° show that in dilute solutions containing hydrochloric acid as catalyst the hydrolysis proceeds in accordance with the equation for a unimolecular change. The velocity co-efficient increases much more rapidly than the hydrogen ion con-centration. The temperature coefficient for 10° is 2·7. The fact that the hydrolysis follows a unimolecular law is in favour of the formula $H_4P_2O_6$ rather than H_2PO_3 for hypophosphoric acid, for the production of phosphorous and phosphoric acids would require the interaction of two molecules of acid if it had the simpler formula.

For the conductivity measurements, pure solutions of the acid were prepared from lead and copper hypophosphate by the action of hydrogen sulphide at low temperatures. The metallic sulphides were filtered off and the excess of hydrogen sulphide removed by a current of air. The conductivity of the solutions after complete hydrolysis was also determined.

The molecular conductivity at 25° referred to the formula $H_4P_2O_6$ increases from $\Lambda = 384·7$ at $v = 32$ to $\Lambda = 629·3$ at $v = 1024$. After hydrolysis, the conductivity of the stronger solutions is diminished, whilst that of the more dilute solutions is increased.

Attention is directed to the resemblance between the properties of hypophosphoric acid and pyrophosphoric acid. This resemblance is found in the conductivity of the solutions, in the behaviour towards indicators, and in their solubility relations, and may be adduced in support of the formula $H_4P_2O_6$ for hypophosphoric acid.   H. M. D.

Preparation of Amorphous Boron. WILHELM KROLL (*Zeitsch. anorg. Chem.*, 1918, **102**, 1—33).—The paper gives the results of numerous experiments on the reduction of boron compounds. Aluminium is unsuitable. Sodium yields mixtures of the lower oxides of boron mixed with boride. Calcium produces only borides. Magnesium may be used for the reduction of boric acid, but the product contains more than 3% Mg in the form of in-soluble boride. The halogen compounds of boron can be reduced by potassium, sodium, magnesium, and aluminium; in each case, borides of the metal are formed as well as free boron. The purest boron is obtained by the reduction of boron chloride with hydrogen in the high tension electric arc. Red phosphorus does not reduce boric acid.

When boric acid is heated with magnesium nitride, a *boron nitride*, probably B_3N, is produced. Boron nitride, BN, can be conveniently prepared from boric acid and calcium cyanamide.

When boron chloride is passed over red phosphorus in the presence of oxygen, a *phosphate*, $2B_2O,P_2O_5$, is formed. Other phosphates appear to exist.

The original contains details as to analytical processes regarding compounds of boron. [See, further, *Ind.*, 148A.]   R. V. S.

Nomenclature of Silicon Compounds. ALFRED STOCK (*Ber.*, 1917, **50**, 1769—1771. Compare A., 1917, ii, 204).—The author again emphasises the fact that very little chemical similarity exists between silicon and carbon compounds of the same structure, and proposes to abandon the nomenclature of carbon chemistry as far as possible. For example, the radicle –SiO·OH in no way resembles a carboxyl group, and therefore the term "hydroxyoxo" is suggested in such a case.   J. C. W.

Silicon Hydrides. II. Bromination of Monosilane, SiH_4. SiH_3Br and SiH_2Br_2. ALFRED STOCK and CARL SOMIESKI (*Ber.*, 1917, **50**, 1739—1754. Compare A., 1916, ii, 319). —The experiments, fully described in this paper, had for their object the bromination of pure silane under conditions favourable to the production of the lower bromides. Under ordinary conditions, the reaction between bromine and silane is very violent, but if an excess of the gas is led into a large vessel on the walls of which solid bromine is deposited, and the temperature is maintained at about −80° to −70°, the mono- and di-substitution products can be obtained comparatively free from $SiHBr_3$ and $SiBr_4$.

The apparatus employed is very elaborate (see A., 1917, ii, 442) and the manipulation is a matter of considerable difficulty. For details of the preparations and final fractionations, the original should be consulted.

Bromomonosilane, SiH_3Br, is a colourless gas with a pungent odour, at the same time reminiscent of monosilane. It has m. p. −94°, b. p. +1·9°/760 mm., D^0 1·533, and molecular latent heat of vaporisation 5·83 Cal. It may be preserved over mercury for some time, but it detonates on exposure to the air, giving silicic acid and brown silicon. It reacts with cold water according to the equation $2SiH_3Br + H_2O = 2HBr + (SiH_3)_2O$ (see following abstract), whilst it may be analysed by measuring the volume of hydrogen produced under treatment with 30% sodium hydroxide, according to the equation $SiH_3Br + 3NaOH = 3H_2 + NaBr + Na_2SiO_3$.

Dibromomonosilane, SiH_2Br_2, is a colourless, mobile, highly refractive liquid, m. p. −70·1°, b. p. 66°/760 mm. (extrapolation; highest recorded value, 18°/123 mm.), D^0 2·17, molecular latent heat of vaporisation 7·41 Cal. In carefully dried vessels, it may be kept for a long time, but it inflames in the air. It is very sensitive to moisture, being decomposed into hydrogen bromide and a solid, $(SiH_2O)_x$. Alkalis decompose it according to the equation $SiH_2Br_2 + 4NaOH = 2H_2 + 2NaBr + Na_2SiO_3 + H_2O$.
                                                J. C. W.

Silicon Hydrides. III. Disiloxane, $(SiH_3)_2O$; Tetrachloromonosilane, $SiCl_4$; Hexachlorodisiloxane, $(SiCl_3)_2O$. ALFRED STOCK, CARL SOMIESKI, and ROBERT WINTGEN (*Ber.*, 1917, **50**, 1754—1764).—When bromomonosilane is shaken with water, it changes into *disiloxane*, $(SiH_3)_2O$, the preparation and purifica-

tion of which are now described. It is a colourless, odourless gas
which does not inflame spontaneously, but burns with a brilliant
light, giving a white smoke and a deposit of brown silicon. It
has m. p. -144°, b. p. $-15\cdot2^\circ$, D-^{80} $0\cdot881$, molecular latent heat
of vaporisation $5\cdot63$ Cal. (compare SiH_4, $3\cdot03$; Si_2H_6, $5\cdot18$; Si_3H_8,
$7\cdot13$; Si_4H_{10}, $9\cdot18$ Cal.). The m. p. and b. p. are lower than the
constants for the parent hydride, Si_2H_6 (m. p. $-132\cdot5^\circ$, b. p.
-15°), which is the reverse of the relationships between ethane and
dimethyl ether. It only decomposes rapidly under the influence
of heat when raised to redness. Submitted to a discharge of electric
sparks, it slowly yields pure hydrogen. When mixed with oxygen,
it inflames or explodes at once, the alteration in volume being in
accordance with the equation $(SiH_3)_2O + 3O_2 = 2SiO_2 + 3H_2O$. It
is not appreciably soluble in water, but soon decomposes into
hydrogen and insoluble products, like $(SiH_2O)_x$, etc. With sodium
hydroxide, however, decomposition is complete, according to the
equation $(SiH_3)_2O + H_2O + 4NaOH = 2Na_2SiO_3 + 6H_2$, which may
be applied in the analysis of the gas.

Disiloxane and chlorine react very vigorously at -125°; the
primary product, hexachlorodisiloxane, may be isolated, but most
of it decomposes according to the equation $4(SiCl_3)_2O = 2SiO_2 +
6SiCl_4$, and some brown silicon is even formed as well. "*Tetra-
chloromonosilane*" (silicon tetrachloride) has m. p. $-68\cdot7^\circ$, b. p.
$56\cdot8^\circ/760$ mm., molecular latent heat of vaporisation $7\cdot19$ Cal.,
and "*hexachlorodisiloxane*" is now found to have m. p. -33° and
b. p. $137^\circ/760$ mm.

It is an interesting fact that disiloxane is the first volatile com-
pound of silicon, hydrogen, and oxygen. Many derivatives, with
the same elements, are known, such as "silicoformic anhydride,"
$(O\!:\!SiH)_2O$, but these must assuredly be polymerides, whereas alkyl,
alkoxyl, and similar derivatives of the true monomeric type, for
example, $(SiR_3)_2O$ and $[Si(OR)_3]_2O$, have frequently been prepared
(compare Martin and Kipping).

Apparently, the compound $SiH_3 \cdot OH$, which would be the
primary product of the action of water on SiH_3Br, is very unstable.
It is noteworthy that the alkyl derivatives, $SiR_3 \cdot OH$, also change
into oxides readily, but the alkyl groups do confer a measure of
stability on them, for hexaphenyldisiloxane, $(SiPh_3)_2O$, changes
back into $SiPh_3 \cdot OH$ on boiling with alcoholic potassium hydroxide
(Kipping and Lloyd, T., 1901, **79**, 455).   J. C. W.

Silicon Hydrides. IV. Oxomonosilane (Protosiloxane).

ALFRED STOCK, CARL SOMIESKI, and ROBERT WINTGEN (*Ber.*, 1917,
50, 1764—1769).—Dibromomonosiloxane reacts with water to form
hydrogen bromide and a volatile compound, which is very probably
oxomonosilane (protosiloxane), $SiH_2\Theta$. The authors have not been
able to isolate this, as it is about as volatile as the hydrogen bromide
solution, and, furthermore, polymerises most readily, so that after
a few distillations the whole of the original silicon is found in the
insoluble residues. The *polymeride* is an amorphous, white solid,

which is stable at 300° (vacuum) or in contact with boiling water, but inflames in the air or chlorine, and reacts with sodium hydroxide according to the equation $(SiH_2O)_x + 2NaOH \longrightarrow 2H_2 + Na_2SiO_3$.   J. C. W.

Proof of the Production of Water in the Formation of Salts from Acid and Base. W. FRANCK (*Zeitsch. physikal Chem. Unterr.*, **30**, 147; from *Chem. Zentr.*, 1917, ii, 358—359).—In the experiment described by Zeitler (A., 1917, ii, 463), calcium or barium hydroxide should be used, as the alkali hydroxides are never anhydrous.   R. V. S.

The System Lithium Sulphate–Lithium Chloride–Water at 30°. F. A. H. SCHREINEMAKERS and G. M. A. KAYSER (*Chem. Weekblad*, 1918, **15**, 120—121).—The solubility of lithium sulphate in water is much diminished by the presence of lithium chloride.   A. J. W.

The Necessity for Applying a New Correction to the Atomic Weight of Silver. PH. A. GUYE (*J. Chim. phys.*, 1917, **15**, 549—560).—The author discusses the various sources of error, due to the presence of occluded gases and the adherent pellicle of moisture on the metal, in the atomic weight determinations of silver. On the basis of recent work (compare A., 1916, ii, 432), he considers that the atomic weight of silver should be revised to 107·87, and that the correct values for the halogens should be $Cl = 35·461$, $Br = 79·925$, $I = 126·915$.   W. G.

Metallographic Investigation of the System Zinc and Selenium. MASUMI CHIKASHIGE and ROKURO KUROSAWA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 245—248).—When zinc and selenium are heated together at a sufficiently high temperature, the compound ZnSe is formed. Zinc selenide has a brilliant yellow colour, D^{21} 5·29, and does not fuse up to 1100°. The fused elements are not appreciably miscible, and the selenide does not dissolve in either. If a fused mixture is allowed to cool, the two free elements and the compound are detectable in the solidified product when examined under the microscope. [See *Ind.*, 153A.]   H. M. D.

Metallographic Investigation of the System Cadmium and Selenium. MASUMI CHIKASHIGE and RIICHI HIKOSAKA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 239—244).—Cadmium and selenium combine to form the compound CdSe, which is infusible up to 1350° and has D^{16} 5·81. The reaction between the elements begins to be appreciable at about 360°, and its velocity increases with rise of temperature. The cadmium selenide does not dissolve in either of the molten elements, which are themselves practically immiscible. When, therefore, a mixture of the two elements is fused and cooled, the product consists of a mixture of cadmium selenide, cadmium, and selenium, which are readily recognised under the

microscope. The proportion of the compound in the product depends on the temperature to which the mixture has been heated and on the length of the period of heating. [See *Ind.*, 153A.]

H. M. D.

The System, Copper Chloride-Lithium Chloride-Water at 30°. F. A. H. SCHREINEMAKERS and (MISS) A. C. NOORDUYN (*Chem. Weekblad*, 1918, **15**, 118—120).—An application of Schreinemakers's graphic method to solutions containing cupric and lithium chlorides. A. J. W.

The Critical Constants of Mercury. E. ARIÈS (*Compt. rend.*, 1918, **166**, 334—337).—Using the formula previously given (compare this vol., ii, 61) for monatomic vapours, and taking the known vapour pressures of mercury at different temperatures, the author calculates the critical temperature of mercury as 1077° and the critical pressure as 420 atmos., these values being a close approximation to the correct figures. W. G.

Preparation, Properties, and Analysis of "White Precipitate." I. M. KOLTHOFF (*Pharm. Weekblad*, 1918, **55**, 208—218).—A comparison of the methods for preparing "white precipitate" given in the Dutch, German, English, Belgian, Swiss, and U.S.A. pharmacopœias. The author is of opinion that the Dutch method is the most satisfactory. [See, further, *Ind.*, April.]

A. J. W.

The Space Lattice of Aluminium. P. SCHERRER (*Physikal. Zeitsch.*, 1918, **19**, 23—27).—The method described by Debye and Scherrer (A., 1917, ii, 437) for the X-ray examination of crystal structure has been applied to finely powdered aluminium. The interference photographs afford evidence that aluminium forms cubic crystals, and that the atoms are arranged according to a simple face-centred lattice. Measurements of the interference patterns give 4.07×10^{-8} cm. for the length of the edge of the elementary cube. The corresponding values obtained from previous investigations are: copper 3.61, silver 4.06, gold 4.07, and lead 4.91×10^{-8} cm.

In spite of the close agreement between the values of the lattice constants and of the atomic volumes for aluminium and gold, the two metals do not form a complete series of mixed crystals. This is attributed to the preponderating influence of chemical affinity.

H. M. D.

The Effect of Great Hydrostatic Pressure on the Physical Properties of Metals. ZAY JEFFRIES (*J. Inst. Metals*, 1917, **18**, 243—252).—The statement of Hanriot (A., 1913, ii, 112) that metals subjected to hydrostatic pressures of the order of 10,000 kilos. per sq. cm. are permanently hardened without deformation, is contrary to modern views on hardness. A repetition of the experiments, using aluminium and an alloy of aluminium and copper,

immersed in light petroleum under pressures up to 12,400 kilo. per sq. cm., shows that no increase in hardness is produced. Hanriot used vaselin, which becomes solid under very high pressures, so that the pressure applied is not hydrostatic. Experiments with the same metals show that a degree of cold deformation, insufficient to cause a noticeable change in the dimensions, produces a marked increase in the hardness as determined by the scleroscope. This explanation is more probable than that of the occurrence of allotropic change in the metal. [See *Ind.*, April.]

C. H. D.

Metallographic Investigation of the System, Aluminium and Selenium. MASUMI CHIKASHIGE and TSUGIJI AOKI (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 249—254).—Cooling curve observations show the formation of a compound, Al_3Se_4, which melts at about 950°. The formation of this compound by heating the two elements together is frequently accompanied by an explosion unless the mixture contains more than 90% of selenium. The compound crystallises out from all fused mixtures of the two elements, and in accordance with this, the two branches of the compound curve on the freezing-point diagram cover the whole of the region from pure aluminium to pure selenium. The eutectics are therefore very nearly coincident with the freezing points of the two elements. The microcrystalline structure of solidified mixtures is in agreement with the thermal data.

Aluminium selenide decomposes in contact with moist air with the formation of hydrogen selenide and aluminium hydroxide. [See *Ind.*, 153A.]   H. M. D.

Metallographic Investigation of the System, Tellurium and Aluminium. MASUMI CHIKASHIGE and JITSUZO NOSÉ (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 227—232).—When aluminium and tellurium are heated together, combination takes place with explosive violence, and the compound Al_2Te_3, m. p. 895°, is formed. This telluride forms mixed crystals with tellurium, the series extending from the pure compound (12·4% by weight of aluminium) to a mixture which contains 4·4% of aluminium. On cooling, the α-mixed crystals undergo transformation into β-mixed crystals. The temperature at which this conversion takes place diminishes with increase in the tellurium content, and for the saturated α-mixed crystals falls to 541°. The β-mixed crystals and tellurium co-exist at the eutectic temperature 414°, the eutectic mixture containing 2·8% of aluminium.

The freezing-point curve of the compound Al_2Te_3 on the aluminium side is terminated by a eutectic point, in which the telluride and aluminium co-exist in equilibrium. The eutectic mixture contains 97% of aluminium and the eutectic temperature is 621°.

The conglomerates, consisting of the telluride or aluminium and the eutectic, undergo transformation when the temperature has

fallen to 551°, with the formation of Al_5Te, according to the equation $Al_2Te_3 + 13Al = 3Al_5Te$.

The telluride, Al_2Te_3, is energetically decomposed by water or by contact with moist air, with the formation of hydrogen telluride and aluminium hydroxide, according to the equation $Al_2Te_3 + 3H_2O = 3TeH_2 + Al_2O_3$. The compound Al_5Te is less readily decomposed, but hydrogen telluride is liberated in contact with water, the reaction being possibly represented by $Al_5Te + H_2O + O_2 = TeH_2 + Al_2O_3 + 3Al$.

Microphotographs are given which afford evidence in support of the results obtained by the thermal analysis of the system. [See *Ind.*, 153A.]

H. M. D.

A Criterion for Allotropic Transformations of Iron at High Temperatures.

KÔTARÔ HONDA (*Sci. Rep. Tohoku Imp. Univ.*, 1917, **6**, 213—217).—The transformations of iron consist in part of allotropic changes which take place at a definite temperature and of gradual changes in which the equilibrium condition is a continuous function of the temperature. The available data relating to these transformations show that A_2 is of the second type, whilst A_3 and A_4 are allotropic changes.

In the case of carbon steels, there are in addition the changes designated by A_0 and A_1, the former representing a gradual change in cementite, and the latter a eutectic transformation of cementite and ferrite which occurs at a definite temperature. H. M. D.

The Micro-structure of Commercially Pure Iron between Ar_3 and Ar_2.

W. J. BROOKE and F. F. HUNTING (*J. Iron Steel Inst.*, 1917, **96**, 233—250).—Armco iron, a basic open-hearth product containing as much as 99·84% Fe, passes through a characteristic brittle range between 900° and 800°, but only during cooling, no change being observed within this range during heating. Quenching experiments show that a eutectic or eutectoid structure appears between these temperatures, but is absent either above or below the brittle range. This constituent resembles pearlite in structure, but is not related to the carbon content, and is also independent of the quantity of oxide in the iron. Heating in hydrogen is without influence on the structure. Similar results are obtained with Swedish iron containing about 0·04% of carbon. [See, further, *Ind.*, 1917, 1096.] C. H. D.

The Nature of Subsidiary Valencies. XVII. Prediction of the Decomposition Temperatures of Ammines.

FRITZ EPHRAIM and ELIAS ROSENBERG (*Ber.*, 1918, **51**, 130—136).—It was recently shown that the ratio of the temperatures cf dissociation for certain pairs of compounds of two elements is roughly constant (A., 1917, ii, 531). If the dissociation points of a number of compounds of one element are known, and the ratio has been determined in the case of one pair of corresponding compounds for another element, then the dissociation temperatures of all the other compounds of the second element can be predicted. This is illus-

trated further in the case of the hexammines of nickel and cobalt salts. The ratio, or "temperature-modulus of the tension," calculated from the dissociation temperatures of the iodides, is Ni/Co, $1/1·075$ (A., 1912, ii, 546). Dividing the known temperatures for other nickel salts by $1·075$, therefore, gives approximately the dissociation points for the corresponding cobalt salts. In the cases of the hexammines of the bromides, nitrates, dithionates, chlorides, sulphates, acetates, and hydrogen carbonates (descending order of stability), the calculated values agree with the observed ones within the limits of the experimental errors.

Most of the hexammines mentioned have been described before (A., 1913, ii, 496, 1061), but the following are new: *cobalt-hexammine nitrate*, by warming the crystalline nitrate in ammonia gas, *dithionate, hypophosphite, formate*, and *acetate*; the dissociation temperatures are respectively 160°, 157·5°, 51°, 21·5°, and 55·5°.   J. C. W.

Metallographic Investigation of the System, Selenium and Antimony. MASUMI CHIKASHIGE and MASASUKE FUJITA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 233—237).—Cooling-curve data show that antimony and selenium form a compound, Sb_2Se_3, melting at 572°. With antimony, the compound forms a eutectic mixture containing 46·5% of selenium, the eutectic temperature being 497°. The eutectic on the selenium side of the compound corresponds very nearly with pure selenium melting at 211°.

Microscopic investigation of solidified mixtures of the two elements confirm the results obtained in the thermal analysis. [See *Ind.*, 153A.]   H. M. D.

Mineralogical Chemistry.

Composition of Seleniferous Sulphur. GLENN V. BROWN (*Amer. Min.*, 1917, **2**, 116—117. Compare A., 1916, ii, 531).—Examination of further specimens of so-called selen-sulphur from various localities (Sicily, Lipari, and New Zealand) by the method of W. Smith (A., 1915, ii, 839) shows the presence of only small amounts of selenium (trace—0·298%). The depth of colour of the material bears no relation to the amount of selenium present; pale yellow specimens may contain more of this element than deep brown ones.   L. J. S.

Epiboulangerite from Montana. EARL V. SHANNON (*Amer. Min.*, 1917, **2**, 131—132).—Bunches of steel-grey needles and fibrous masses occur with quartz and granular blende in the Iron Mountain mine, near Superior, Montana. Small grains and needles are also scattered through the blende. Associated minerals

in small amounts are chalybite, pyrites, and sericite. The fibres are moderately brittle and break across at right angles; the streak is blackish lead-grey. D 6·303. A partial analysis gave Pb 52·74, Sb 20·85%. From these characters, the mineral is provisionally identified as epiboulangerite. L. J. S.

Mullanite, a New Member of the Jamesonite Group, from Two Localities. EARL V. SHANNON (*Amer. J. Sci.*, 1918, [iv], **45**, 66—70).—In the Iron Mountain mine near Superior, Montana, the new mineral occurs with epiboulangerite (preceding abstract), from which it is indistinguishable in appearance; but it is readily distinguished by its brownish-black streak, that of the epiboulangerite being greyish-black. It here forms long, parallel, steel-grey fibres around and enclosed in a crystal of quartz. In the Gold Hunter mine, near Mullan, in Idaho, forty miles W.N.W. of the former locality, the mineral occurs with quartz and chalybite as fine, matted, wool-like masses of dark grey fibres, and as a compact, steel-grey, fibrous material. The needles are usually flattened and are deeply striated longitudinally; they are terminated by the basal plane, and are probably orthorhombic ($a : b =$ 1:0·835) with the three pinacoidal cleavages. The thinner fibres are very flexible, whilst the thicker ones are quite brittle. Analysis I, mean of two of material from the Iron Mountain mine, and II, from the Gold Hunter mine, agree with the formula $5PbS, 2Sb_2S_3$, corresponding with the silver-lead diaphorite.

	Sb.	As.	Pb.	Ag.	Cu.	Fe.	S.	Total.	Sp. gr.
I.	25·71	0·25	55·05	nil	nil	trace	18·82	99·83	6·274*
II.	24·67	0·64	53·33	nil	nil	1·47†	18·11	98·22	6·407

* Probably low. † Representing chalybite 3·4% present as impurity.

L. J. S.

Occurrence of Chalmersite, $CuFe_2S_3$, in the Ore Deposits of Prince of Wales Sound, Alaska. BERTRAND L. JOHNSON (*Econ. Geol.*, 1917, **12**, 519—525).—This mineral, previously known only as minute crystals from Brazil (A., 1902, ii, 267; 1906, ii, 553), has been found in considerable quantities at eight different localities in the Ellamar district and on Knight Island, in Prince of Wales Sound, where it has been mined as an ore of copper. It is massive, very pale yellow, and shows a conspicuous cleavage with a satiny sheen. It is strongly magnetic, and this property enables it to be separated from the copper-pyrites with which it is intimately intergrown. Analyses by E. T. ALLEN agree with the formula $CuFe_2S_3$.

Cu.	Fe.	S.	Sp. gr.
22·67—23·83	40·70—41·92	35·09—35·30	4·04

L. J. S.

Chalcedony Mistaken for an Iron Sulphate Mineral. EDGAR T. WHERRY and MILTIADES L. GLENN (*Amer. Min.*, 1917, **2**, 6—7).—Two specimens of orange-brown botryoidal material had

been for many years labelled as glockerite in the U.S. National Museum. I is from Pinos Altos, New Mexico, and II from Black Hawk, Colorado. When examined, they were found to be chalcedony, and this is confirmed by analyses I and II. The ferric sulphate is not present as visible enclosures, nor is it extracted by acids; it must be present as sub-microscopic inclusions.

	SiO_2.	Fe_2O_3.	SO_3.	H_2O <110°.	H_2O >110°.	Total.	Sp. gr.	n.
I.	94·37	3·10*	1·47	trace	1·86	100·80	2·57	1·530
II.	93·94	1·58	1·00	0·65	2·59	99·76	2·55	1·525

* Including a minute amount of pyrites.

For pure chalcedony $D = 2·60$ and $n = 1·537$; as shown above, with increasing water there is a corresponding decrease in the values for the density and refractive index.   L. J. S.

Massicot and Litharge, the Two Modifications of Lead Monoxide. ESPER S. LARSEN (*Amer. Min.*, 1917, **2**, 18—19).— Natural specimens of 'massicot' from Austria and from Kern Co. and San Bernardino Co., California, consist of minute brownish-red scales built up of two minerals with distinct optical properties. The central portion of the plates consists of the yellow orthorhombic modification (nearly colourless under the microscope, optically biaxial and positive, $\beta = 2·61$, birefringence very strong), and the borders of the red tetragonal modification (yellowish-orange under the microscope, optically uniaxial and negative, $\omega = 2·64$, birefringence very strong). It is proposed to restrict the name litharge to the former and massicot to the latter. The border of massicot is probably an inversion product of the litharge. (Compare A., 1915, ii, 59).   L. J. S.

Nomenclature of the Lead Monoxide Minerals. E. T. WHERRY (*Amer. Min.*, 1917, **2**, 19).—The mineralogical term massicotite for a mineral corresponding with the artificial product massicot was used by D'Achiardi in 1883. Now that the orthorhombic modification of lead monoxide has been recognised as a mineral (see preceding abstract), the name *lithargite* is suggested for the second species.   L. J. S.

Xanthosiderite from Schendlegg, Lower Austria: Formation of Brown "Glaskopf." H. LEITMEIER and M. GOLDSCHLAG (*Centr. Min.*, 1917, 473—477).—Near the foot of the Raxalp, in Lower Austria, are deposits of iron ore consisting of chalybite carrying small amounts of copper-pyrites. In the level of the Schendlegg mine, the walls are coated with a reddish-brown, unctuous, colloidal material of recent formation. After drying in the air for a few weeks, this shows a concentric, shelly structure and brown colour; the streak is yellowish-brown. Under the microscope, it showed thin scales of brownish-yellow, amorphous material. It then contained 19·70% H_2O, corresponding with $Fe_2O_3,2H_2O$—the formula for xanthosiderite. Of this water, 3·93% is lost over sulphuric acid and 8·16% at 100°. The same

material after exposure to the air for two years still contained the same quantity of water (H_2O 19·11, Fe_2O_3 80·02, SiO_2 0·47%), but it had by that time acquired a dark blackish-brown colour with metallic lustre on the surface and a dark brown streak. Under the microscope, the material was now seen to have a distinct granular structure and to be crystalline. The colloidal material has thus become gradually converted to the crystalline, brown "Glaskopf."

L. J. S.

Columnar Manganocalcite from Franklin Furnace, New Jersey. WALLACE GOOLD LEVISON (*Amer. Min.*, 1916, **1**, 5).—This is pinkish-white with a marked columnar structure. It is tough and less brittle than ordinary calcite, and is soluble in cold acid. Analysis gave:

CaO.	MnO.	FeO.	ZnO.	MgO.	CO_2.	Insol.	Total.	Sp. gr.
38·58	11·94	0·22	0·29	4·33	39·70	4·60	99·66	2·81

L. J. S.

Proof that Priceite is a Distinct Mineral Species.
ESPER S. LARSEN (*Amer. Min.*, 1917, **2**, 1—3).—The friable, chalky priceite from Curry Co., Oregon, and the compact, nodular pandermite from Asia Minor have often been regarded as impure, massive varieties of colemanite. A determination of the optical constants of these minerals proves that pandermite is identical with priceite ($\alpha=1·572$, $\beta=1·592$, $\gamma=1·594$), and that the latter is distinct from colemanite ($\alpha=1·586$, $\beta=1·592$, $\gamma=1·614$). Priceite is triclinic, $5CaO,6B_2O_3,9H_2O$, and colemanite monoclinic, $2CaO,3B_2O_3,5H_2O$. On the other hand, fine-grained specimens (labelled priceite) of hydrous calcium borate from Californian localities were found to be howlite.

L. J. S.

Vivianite from the Land Pebble Phosphate Deposits of Florida. THOMAS L. WATSON and STAPLETON D. GOOCH (*J. Washington Acad. Sci.*, 1918, **8**, 82—88).—An examination of a sample of vivianite occurring in a ferruginous or dark yellow, ochreous matrix in a deposit of Florida pebble phosphate. The mineral occurred as light to pale green crystals, D 2·693, an optical examination of which gave the following results: optically $(+)$; $2V$ large; dispersion not strong; X is normal to 010; Z makes an angle of $28°30'\pm1°$ with c. The refractive indices are $\alpha=1·580\pm0·003$; $\beta=1·598\pm0·003$; $\gamma=1·627\pm0·003$. Analysis gave:

FeO.	Fe_2O_3.	CaO.	MnO.	P_2O_5.	TiO_2.	SiO_2.	H_2O (<105°).	H_2O (>105°).	Total.
32·64	9·43	0·02	0·25	29·99	trace	0·12	11·86	15·84	100·15

The presence of ferric oxide in blue vivianite is due to oxidation, and not to inversion. Oxidation takes place rapidly on fine grinding. The matrix in which the vivianite occurs is not a clay, but an earth composed of the hydroxides of iron and aluminium, chiefly the former, phosphates of calcium, iron, and aluminium, and some free quartz.

W. G.

Mirabilite from the Isle Royale Mine, Michigan. ALBERT B. PECH

$(Amer. Min., 1917, 2, 62—63)$.—The material, from the Isle Royale copper mine at Houghton, consists of a clear, colourless mass of interlocking fibres with a little clayey matter enclosed. On exposure to the air, it soon crumbles to a white powder. All the water is expelled at 130°. Deducting 5·69% insoluble, the following analysis agrees with the usual formula, $Na_2SO_4,10H_2O$. Mean refractive index, 1·437.

Na$_2$O.	K$_2$O.	CaO.	SO$_3$.	Cl.	H$_2$O.
19·02	0·77	trace	25·37	trace	54·84

L. J. S.

Gilpinite, a New Uranium Mineral from Colorado.

ESPER S. LARSEN and GLENN V. BROWN $(Amer. Min., 1917, 2,$ 75—79).—The mineral occurs as pale greenish-yellow to canary-yellow aggregates of minute, lath-shaped crystals intermixed with gypsum on pitchblende and copper ore from Gilpin Co., Colorado. The crystals are monoclinic, and show two sets of polysynthetic twin-lamellæ. The optical constants are compared with those of zippeite and uranopilite. The mineral is readily soluble in dilute acids; it is difficultly fusible, and becomes black on heating. $D > 3·32$. The following analysis (19·64% gangue, mainly pitchblende, deducted) gives the formula $RO,UO_3,SO_3,4H_2O$, where $R = Cu, Fe, Na_2$.

SO$_3$.	UO$_3$.	CuO.	FeO.	PbO.	Na$_2$O.	K$_2$O.	H$_2$O at 105°.	H$_2$O at 200°.
15·45	56·72	5·80	4·77	0·82	1·93	0·70	1·66	12·15

A specimen labelled uranopilite from Cornwall was found to have optical characters identical with those of the Colorado mineral, and it is also regarded as gilpinite.

L. J. S.

The Probable Identity of Uranothallite and Liebigite.

ESPER S. LARSEN $(Amer. Min., 1917, 2, 87)$.—Optical examination of three specimens labelled liebigite from Schneeberg, Saxony, and Joachimsthal, Bohemia, and of two specimens labelled uranothallite from the latter locality, gave the following results: optically positive, $2E = 65° ± 3°$, $2V = 42° ± 2°$, $\rho > v$, $a = 1·500$, $\beta = 1·503$, $\gamma = 1·537 ± 0·003$, cleavage normal to a. The single analysis of liebigite (for which the formula was deduced as

$$CaO,UO_3,2CO_2,20H_2O)$$
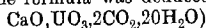
was made in duplicate on only 65 and 85 mg. of material, and although this name has priority, it is rejected in favour of the name uranothallite, which was applied to more completely determined material, and analysed by three authors with the result $2CaO,UO_3,3CO_2,10H_2O$. It is, however, remarked that the original material described as liebigite was not available for optical examination, and it is possible that those examined may really have been uranothallite incorrectly labelled liebigite. L. J. S.

Pectolite Pseudomorphous after Quartz from West Paterson, N.J. MILTIADES L. GLENN (*Amer. Min.*, 1917, **2**, 43—45).—A small group of crystals collected from a basalt quarry at West Paterson, New Jersey, shows the forms of sharply-developed crystals of quartz, each about $\frac{2}{3}$ inch in diameter. They, however, consist entirely of a compact, fibrous material with the optical characters of pectolite. Analysis of the material gave:

SiO_2.	$Al_2O_3 + Fe_2O_3$.	CaO.	MgO.	Na_2O.	H_2O.	Total.
53·42	0·52	32·63	2·35	7·45	3·77	100·14

L. J. S.

A New Occurrence of Stevensite, a Magnesium-bearing Alteration-product of Pectolite. MILTIADES L. GLENN (*Amer. Min.*, 1916, **1**, 44—46).—The Hartshorn quarry at Springfield, Essex Co., New Jersey, is in a somewhat altered basalt containing in cavities secondary anorthoclase, quartz, calcite, zeolites, datolite, and pectolite. Some of the pectolite is of the usual type as silky radiations of fine needles, but much of it is altered, the colour becoming pinker and the lustre more waxy towards the ends of the fibres. In the most altered material the colour is white to pink, lustre waxy, translucent; the structure is compact, and the material optically isotropic and amorphous, n about 1·50; D 2·15—2·20, H $2\frac{1}{2}$. It is easily fusible to a white enamel, and is decomposed by hydrochloric acid with separation of granular silica. Analysis I is of partly altered material still retaining the pectolite structure, but impregnated by waxy material; and II of the most altered waxy material, apparently homogeneous, although still perhaps containing a few fibres of unaltered pectolite:

	SiO_2.	$Al_2O_3 + Fe_2O_3$.	MnO.	CaO.	MgO.	Na_2O.	$H_2O (> 110°)$.	Total.
I.	53·84	1·18	0·13	22·59	9·81	5·59	6·76	99·90
II.	58·03	0·37	0·03	1·61	27·66	3·73	8·45	99·88

These analyses, when arranged in a series with other analyses of altered pectolites ('walkerite' from Corstorphine Hill, Edinburgh, and 'magnesium pektolith' from Burg, Herborn, Germany), show a gradual passage from the monohydrate of pectolite,

$$HNaCa_2(SiO_3)_3 + H_2O,$$
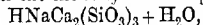
to the monohydrate of talc, $H_2Mg_3(SiO_3)_4 + H_2O$. They show a progressive increase in magnesium and water and a decrease in calcium and sodium. The latter formula, to which anal. II approximates, is given as the composition of stevensite. The alteration has no doubt been brought about by the action of magnesium-bearing solutions derived from the weathering of the basalt.   L. J. S.

A Review of Amorphous Minerals. AUSTIN F. ROGERS (*J. Geol. Chicago*, 1917, **25**, 515—541).—The amorphous equivalents of crystalline minerals should be recognised as separate mineral species and given distinctive names. About twenty of the more prominent and well-defined, amorphous minerals (for example, opal, psilomelane, collophane, halloysite, etc.) are discussed. The amor-

phous cadmium sulphide, probably with adsorbed water, CdS,xH_2O, which occurs as a thin, powdery, yellow coating on zinc-blende, is separated from the hexagonal greenockite and named *xantho-chroite*.

Intimately associated with the chrysocolla (a microcrystalline or crystallised mineral) of several localties is the amorphous equivalent, to which the name *cornuite* is applied. Cornuite from Copper Mountain, Prince of Wales Island, Alaska, occurs as a banded crust of bluish-green, transparent, glassy material with refractive index 1·549. It is more readily soluble in hydrochloric acid than chrysocolla, and is also somewhat softer. Analysis by G. S. BOHART gave:

CuO.	Al_2O_3.	SiO_2.	H_2O.
42·61	0·31	34·13	23·11

Here the ratios of both silica and water are somewhat in excess over those required by the chrysocolla formula, H_4CuSiO_5, and cornuite is probably a solid solution of cupric oxide, silica, and water, $mCuO,nSiO_2,xH_2O$.

The natural hydrocarbons and glasses are discussed under the term mineraloids.   L. J. S.

Nature of the Water in Zeolites. GEORG STOKLOSSA (*Diss. Breslau*, 1917, 64 pp.; from *Chem. Zentr.*, 1917, ii, 420—421).

—The author has investigated the following seven minerals, and has found in all cases that the water contained in them is in chemical combination: (1) heulandite from Teigarhorn, in Iceland; (2) skolezite from Iceland; (3) natrolite from Bohemia; (4) harmotome from Strontian; (5) chabasite from Nova Scotia; (6) analcime from the Seiseralp; (7) apophyllite from the Seiseralp. Analyses gave:

	SiO_2.	Al_2O_3.	BaO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
1.	59·66	16·37	—	6·33	—	2·35	0·42	14·90	100·03
2.	46·71	25·90	—	13·70	—	—	—	13·64	99·95
3.	46·95	27·06	—	0·27	—	—	15·97	9·58	99·73
4.	48·51	16·44	20·19	·—	—	1·59	—	13·79	100·52
5.	48·12	19·27	—	9·63	2·45	3·02	—	16·11	98·59
6.	54·74	23·64	—	0·32	--	—	13·71	8·55	100·96
7.	53·87	—	—	23·85	—	4·81	—	16·24	99·47

         R. V. S.

A New Occurrence of Ptilolite. LOUIS H. KOCH (*Amer. Min.*, 1917, **2**, 143—144).

—This species, previously known only from Colorado, is described from Challis, Idaho. The material consists of a soft, fluffy mass of minute fibres coating a layer of chalcedonic silica on a weathered basic igneous rock. Analysis gave:

	SiO_2.	Al_2O_3.	CaO.	MgO.	K_2O,Na_2O.	H_2O.	Total.
I.	81·5	8·2	1·7	0·3	1·0	7·3	100·0
II.	72·3	12·3	2·6	0·4	1·5	10·9	—

The high value for silica is due to the presence of microscopic spindle-shaped crystals of quartz to the extent of $31\frac{1}{3}\%$; deducting

this, the results are as under II. Under the microscope the material is seen to consist of well-defined, transparent needles with straight optical extinction; biaxial with large angle and optically negative; refractive indices $\alpha = 1\cdot475$, $\beta = 1\cdot477$, $\gamma = 1\cdot478$. D $2\cdot30$. L. J. S.

A Peculiar Clay from near the City of Mexico. E. W. HILGARD (*Proc. National Acad. Sci., U.S.A.*, 1916, **2**, 8—12).—The material examined consisted of soil samples from certain unproductive tracts of land on the hacienda Santa Lucia. It has the appearance of a dark grey clay, adheres strongly to the tongue, and becomes very plastic with a little water. D $2\cdot25$. When immersed in water it swells up to many times (for one sample as much as thirty-two times) its original volume, forming a coherent, gelatinous mass. The larger part of the material is colloidal, but there are also minute, inseparable grains of calcium and magnesium carbonates. A partial analysis gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Ign.	Insol.	Na_2SO_4.	Na_2CO_3.	NaCl.	Total.
43·00	3·48	1·76	9·06	17·11	19·60	1·83	1·74	0·74	0·12	98·44

The material is thus mainly a hydrated magnesium silicate allied to saponite or sepiolite, but it differs from these in being very readily decomposed by acids, even by dilute acetic acid, and in its exceptionally high absorptive power for water. The name *lucianite* is suggested for this new type of magnesian clay.　　　L. J. S.

Analytical Chemistry.

Filtering Tube. WILLIAM M. THORNTON, Jun. (*J. Ind. Eng. Chem.*, 1918, **10**, 132).—The stem of a carbon filter tube is provided with a glass tap, and the top of the tube is closed by a rubber stopper, through which pass the stem of a holder for a filter crucible and an exit tube connected with a pump. The carbon tube serves as a small filter flask; the filtrate collected in this tube is discharged by opening the tap and admitting air through a side-tube on the exit tube. The apparatus is convenient for use in dealing with small quantities of liquid.　　　W. P. S.

Preparation of N/100 Permanganate Solutions. J. O. HALVERSON and OLAF BERGEIM (*J. Ind. Eng. Chem.*, 1918, **10**, 119—120).—To prepared permanent $N/100$-permanganate solution 0·40 gram of potassium permanganate is dissolved in 1 litre of re-distilled water, and the solution is heated nearly at boiling point for thirty-six hours under a reflux apparatus. The solution is then cooled, kept overnight, filtered through asbestos, and after three days standardised against $N/50$-oxalic acid solution (0·1261 gram of crystallised oxalic acid per 100 c.c.). The strength of the solution does not vary more than 0·1% per week. [See, further, *Ind.*, 193A.]
　　　W. P. S.

Suggestions on some Common Precipitations. GEORGE H. BROTHER (*J. Ind. Eng. Chem.*, 1918, **10**, 129—130).—The following directions are given for obtaining precipitates which are retained by filter paper of moderately close texture. In the case of barium sulphate, the sulphate solution should contain about 1 c.c. of hydrochloric acid (D 1·2) per 200 c.c.; it should be heated to boiling, treated with about one-half the required quantity of barium chloride solution, added drop by drop, and the remainder of the barium chloride is added after the lapse of five minutes. The mixture is ready for filtration after a further fifteen minutes' digestion.

Calcium oxalate is readily obtained in a crystalline state by treating the boiling solution of the calcium salt with an excess of ammonium oxalate, dissolving the precipitate by adding a very slight excess of hydrochloric acid, then adding ammonia drop by drop until the precipitate has formed again, and keeping the mixture hot for thirty minutes.

For the precipitation of ammonium phosphomolybdate, the phosphate solution is rendered ammoniacal, then acidified with nitric acid, heated to boiling, and treated at this temperature with ammonium molybdate solution. When a phosphate is precipitated with magnesia mixture, the precipitate should be dissolved by the addition of hydrochloric acid, the solution heated to boiling, and ammonia then added slowly until a distinctly crystalline precipitate has formed; the mixture is now cooled, one-fifth of its volume of ammonia (D 0·9) is added, and, after fifteen minutes, the precipitate is collected on a filter.   W. P. S.

Reagents for Use in Gas Analysis. VI. The Absorption of Hydrogen by Sodium Oleate. R. P. ANDERSON and M. H. KATZ (*J. Ind. Eng. Chem.*, 1918, **10**, 23—24. Compare A., 1917, ii, 39).—The sodium oleate reagent containing nickel in suspension, recommended by Bosshard and Fischli for the absorption of hydrogen (A., 1915, ii, 788), is of little use. Amongst the objections to the reagent may be mentioned the time and trouble required for the preparation of the catalyst and the readiness with which it oxidises, the bad keeping properties of the reagent itself, and the slowness of the absorption of the hydrogen. [See further, *Ind.*, 82A.]   W. P. S.

Detection and Estimation of Small Quantities of Free Hydrochloric Acid in the Presence of Chlorides and other Mineral or Organic Acids. M. ENTAT (*Ann. Chim. anal.*, 1918, **23**, 5—7).—Hydrochloric acid may be determined by the electrometric titration method previously described (A., 1917, ii, 268). N-Silver nitrate solution is used for titration, and the hydrochloric acid solution should contain 2% of nitric acid.   T. F. B.

Titration of Chlorides by Volhard's Method. J. M. KOLTHOFF (*Zeitsch. anal. Chem.*, 1917, **56**, 568—576).—Trustworthy results may be obtained in this method if, as recommended by Schoorl, the titration is interrupted at the first change in colour

ot the indicator, the mixture then stirred thoroughly, and the titration completed. Rothmund's modification (A., 1909, ii, 932) is less trustworthy. The author finds that it is best to dilute the solution containing the chloride and an excess of silver nitrate to a definite volume, shake the mixture thoroughly, allow the precipitate to settle, and titrate an aliquot portion of the clear solution with thiocyanate. As the silver chloride absorbs about 0.7% equivalent of silver, a corresponding correction of 0.7% must be made on the quantity of chloride found. Chlorides may be detected and estimated in the presence of thiocyanates if the latter be oxidised by treatment with sodium peroxide in sulphuric acid solution (if hydrogen peroxide is used it should be tested previously for the presence of chlorides). W. P. S.

Estimation of Chlorates and Hypochlorites. E. RUPP (*Zeitsch. anal. Chem.*, 1917, **56**, 580—586).—Ten c.c. of a solution containing about 0.5% of potassium chlorate and calcium hypochlorite are placed in a stoppered litre flask, diluted to 100 c.c., 2 grams of potassium iodide are added, the mixture is acidified with dilute acetic acid, and, after five minutes, it is titrated with $N/10$-thiosulphate solution; this titration gives the quantity of hypochlorite present. Another portion of 10 c.c. of the solution is also placed in a large stoppered flask, and 1 gram of potassium bromide and 30 c.c. of concentrated hydrochloric acid are added. After fifteen minutes, the mixture is treated with 150 c.c. of 1% potassium iodide solution, shaken, and titrated with $N/10$-thiosulphate solution. The difference between the two titrations corresponds with the amount of chlorate in the solution. W. P. S.

Action of Sodium Sulphide on Iodine and the Use of the Reaction in Analysis. JOSEF EHRLICH (*Zeitsch. anal. Chem.*, 1918, **57**, 21—22).—Pure sodium sulphide solution reacts with free iodine to form sodium iodide; sulphur is liberated at the same time, but re-dissolves in the excess of sodium sulphide added. The iodine in an iodide solution also containing other substances may be estimated by liberating the iodine with potassium permanganate, adding an excess of sodium sulphide, separating the manganese sulphide, etc., by filtration, removing the excess of sulphide in the filtrate by treatment with zinc sulphate, and then precipitating the iodine as silver iodide. W. P. S.

Estimation of Hypobromite and Bromate, or Hypoiodite and Iodate, in Mixtures of the Same. E. RUPP (*Zeitsch. anal. Chem.*, 1918, **57**, 16—19).—The method is based on the reaction between hypobromites or hypoiodites and hydrogen peroxide, according to the equation $NaBrO + H_2O_2 = NaBr + H_2O + O_2$. The solution containing hypobromite and bromate is treated with a mixture of hydrogen peroxide and sodium hydroxide solution, the excess of the hydrogen peroxide is then removed by boiling, potassium iodide and sulphuric acid are added, and the iodine liberated by the bromate is titrated with thiosulphate solu-

8*—2

tion. Another portion of the solution is treated directly with potassium iodide and sulphuric acid and titrated with thiosulphate solution. This titration is a measure of the hypobromite and bromate together, and the quantity of hypobromite present is obtained from the difference in the two titrations. A mixture of hypoiodite and iodate is analysed in the same way.   W. P. S.

Estimation of Iodates in the Presence of Bromates. E. RUPP (*Zeitsch. anal. Chem.*, 1918, **57**, 19—21).—Bromates, when treated with dilute hydrochloric acid, are decomposed gradually with the formation of hydrobromic and hypochlorous acids, whilst iodates are not affected by this treatment. To estimate the two salts when contained in the same solution, a portion of the latter is treated with potassium iodide and sulphuric acid and titrated, after a few minutes, with thiosulphate solution. Another portion of the solution is diluted with water to 50 c.c., 20 c.c. of 12·5% hydrochloric acid are added, and, after one hour, the mixture is treated with 25 c.c. of 3% hydrogen peroxide solution and 15 c.c. of 15% sodium hydroxide solution, boiled for ten minutes, cooled, and titrated with thiosulphate solution after the addition of potassium iodide and sulphuric acid. The first titration gives the quantities of bromate and iodate together, and the difference between the two titrations corresponds with the quantity of bromate present.   W. P. S.

Estimation of Sulphur in Pyrites. Z. KARAOGLANOW [with P. and M. DIMITROW] (*Zeitsch. anal. Chem.*, 1917, **56**, 561—568). —After the sulphur has been oxidised to sulphuric acid by heating with a mixture of nitric and hydrochloric acids, or by fusion with sodium carbonate and potassium nitrate, the sulphuric acid may be precipitated directly from the hydrochloric acid solution obtained after separating the silica, previous removal of the iron being unnecessary if the precipitation is carried out under the following conditions. The solution (from 0·5 gram of pyrites), which should contain from 30 to 50 c.c. of $6N$-hydrochloric acid (free), is diluted to 700 c.c., heated to boiling, and 40 c.c. of hot 10% barium chloride solution diluted previously with 100 c.c. of hot water are added gradually while the mixture is stirred. The precipitated barium sulphate is collected after fifteen hours, washed first with water containing hydrochloric acid and barium chloride, then with hot water, dried, ignited, and weighed.   W. P. S.

Gravimetric Estimation of Sulphuric Acid and Barium as Barium Sulphate. II. Z. KARAOGLANOW (*Zeitsch. anal. Chem.*, 1917, **56**, 487—498. Compare this vol., ii, 47).—In the estimation of barium, the presence of nitric acid or a large quantity of hydrochloric acid causes the results obtained to be too low; potassium salts and ferric chloride have the opposite effect. Under equal conditions, the errors in the gravimetric estimation of barium are less than in the estimation of sulphuric acid   W. P. S.

Detection of Selenium in Sulphuric Acid. LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1917, **5**, 121—123).— Sulphuric acid containing selenium gives an intense violet coloration with aspidospermine. The pure acid does not give this reaction, but in presence of an oxidiser, such as potassium chlorate or lead peroxide, it develops a rose-red coloration. [Compare *Ind.*, 147A.] A. J. W.

Estimation of Nitrogen in Calcium Cyanamide. (MLLE.) BRONISLAVA TURKUS (*Ann. Chim. anal.*, 1918, **23**, 3—5).—In the estimation of nitrogen in cyanamide by Kjeldahl's method, only thirty minutes' digestion with sulphuric acid is required for the complete decomposition of the cyanamide if the sulphuric acid used is diluted previously with one-fourth of its volume of water; for 1 gram of the sample, 40 c.c. of concentrated sulphuric acid mixed with 10 c.c. of water are required. The digestion must be prolonged for more than thirty minutes if the acid used is weaker or stronger than the concentration given. W. P. S.

The Microchemical Estimation of Nitrogen. B. SJOLLEMA and C. W. G. HESSERSCHY (*Biochem. Zeitsch.*, 1917, **84**, 359—370). —A critical examination of the methods of Bang and of Folin and Denis, with some suggested minor alterations of the details. S. B. S.

Simple Rapid Method of Estimating the Filtrate Nitrogen in Small Quantities of Blood and of other Body Fluids. R. DONALD (*Quart. J. Med.*, 1917, **11**, 19—29).—One c.c. of blood is mixed with 1 c.c. of a saturated solution of sodium chloride in a mixture of nine parts of 6% sulphuric acid and one part of 6% phosphoric acid. It is centrifugalised, and 1 c.c. of the clear liquid is then transferred to a second centrifugal tube, mixed with 0·1 c.c. of 10% phosphomolybdic acid, and again centrifugalised. Of the final clear, protein-free liquid, 1 c.c. is injected into a solution of sodium hypobromite contained in a Doremus ureometer, and the nitrogen evolved is transferred to a calibrated narrow measuring tube and its volume measured. Attention is directed to the necessity of rapping the ureometer prior to the removal of the nitrogen to the measuring tube in order to liberate a considerable proportion of the gas, which otherwise remains in the gas-supersaturated hypobromite solution. The result is obtained in about forty-five minutes from the commencement of the operations, and is stated to be sufficiently accurate for clinical purposes. H. W. B.

Estimation of Amino-acid Nitrogen in the Blood. SEIZABURO OKADA (*J. Biol. Chem.*, 1918, **33**, 325—331).—The chief point in the new method is the removal of the proteins of the blood by heating with dilute acetic acid, the last traces of protein being removed by shaking with kaolin. The use of alcohol as a precipitant is shown to be undesirable (compare Bock. A.. 1917, ii, 159). H. W. B.

The Estimation of Residual Nitrogen of the Blood. B. SJOLLEMA and C. W. G. HESSERSCHY (*Biochem. Zeitsch.*, 1917, **84**, 371—377).—Different results are obtained according to whether phosphomolybdic acid, metaphosphoric acid, or trichloroacetic acid is used as precipitant of the proteins.   S. B. S.

Still-head for Use in the Distillation of Ammonia. A. HUTIN (*Ann. Chim. anal.*, 1917, **22**, 242—244).—The apparatus consists of a bulb with a lower tube which enters the neck of the distillation flask, and an upper tube connected with a receiver; this upper tube extends into the bulb, the portion inside the bulb being constricted and bent upwards. If desired, a wide tube filled with glass beads may be placed between the lower tube of the still-head and the distillation flask. The whole apparatus is made of sheet tin, and its purpose is to prevent any spray from the distillation flask passing over into the receiver.   W. P. S.

Use of Diphenylamine-Sulphuric Acid for Colorimetric Estimations. J. TILLMANS (*Zeitsch. anal. Chem.*, 1917, **56**, 509—511).—A reply to L. Smith (A., 1917, ii, 217). The use of diphenylamine for the colorimetric estimation of nitric acid is trustworthy if the test solution and the standards are treated in exactly the same way, particularly as regards shaking or stirring.
                                                            W. P. S.

Estimation of Phosphorous, Hypophosphoric, and Phosphoric Acids in Mixtures. R. G. VAN NAME and WILBERT J. HUFF (*Amer. J. Sci.*, 1918, [iv], **45**, 91—102).—The estimation of phosphorous acid in presence of hypophosphoric and phosphoric acids may be effected by the absorption of iodine in presence of disodium hydrogen phosphate.

The same method may be used for the estimation of hypophosphoric acid if this is hydrolysed in presence of hydrochloric acid as catalyst, producing thereby equimolecular quantities of phosphorous and phosphoric acids in accordance with the equation $H_4P_2O_6 + H_2O = H_3PO_3 + H_3PO_4$.

A mixture of phosphorous, hypophosphoric, and phosphoric acids may be analysed by estimating the phosphorous acid before and after hydrolysis by the iodometric method, and also determining the total phosphoric acid in the solution after oxidation. . [See, further, *Ind.*, 147A.]   H. M. D.

The Precipitation of Phosphoric Acid in the State of Ammonium Phosphomolybdate. Estimation of Phosphoric Acid by a Simple Azotometric Method. J. CLARENS (*Compt. rend.*, 1918, **166**, 259—262).—If the phosphate is precipitated by ammonium molybdate in the presence of sufficient ammonium nitrate, the resultant precipitate contains phosphoric acid and ammonia in the proportions requisite to form triammonium phosphate. The proportions to use should be 0·1 gram of phosphoric anhydride and 100 c.c. of ammonium molybdate containing 15—20 grams of ammonium nitrate. The precipitate is washed with dis-

tilled water, and the ammonia present estimated by one of the usual methods, such as distillation with potassium hydroxide.

W. G.

Estimation of Phosphoric Acid. A Modification of the Citrate Method. J. GROSSFELD (*Zeitsch. anal. Chem.*, 1918, **57**, 28—33).—To avoid the intermediate precipitation of phosphoric acid by molybdic acid, the author proposes a method for the analysis of fertilisers, ashes, etc., in which the calcium is precipitated as oxalate from an acetic acid solution, and, after the removal of the calcium oxalate, the phosphoric acid is precipitated in the usual way as ammonium magnesium phosphate, citric acid being added to prevent precipitation of iron and aluminium. The hydrochloric acid solution (or other solution) of the substance under examination is treated with a few drops of methyl-orange solution and an excess of ammonium oxalate solution, and saturated ammonium acetate or sodium acetate solution is added until the colour of the indicator changes from red to yellow; the mixture is then diluted to 100 c.c., mixed, and filtered through a kieselguhr filter. An aliquot portion of the filtrate is mixed with 5 c.c. of 20% citric acid solution and the phosphoric acid precipitated with magnesia mixture.

W. P. S.

Estimation of Phosphoric Acid, particularly in Superphosphate. G. VORTMANN (*Zeitsch. anal. Chem.*, 1917, **56**, 465—487).—For the direct estimation of phosphoric acid in superphosphate, the most trustworthy method consists in precipitation as ammonium magnesium phosphate after the calcium has been removed as oxalate and the iron as sulphide; the presence of ammonium oxalate, ammonium molybdate, and ammonium sulphide does not interfere with the precipitation. If aluminium salts are present, the quantity of magnesia mixture used should be increased. When the phosphoric acid is precipitated with molybdic acid solution before it is converted into ammonium magnesium phosphate, the precipitation may be made equally well from a nitric, hydrochloric, or sulphuric acid solution. Molybdic acid solution containing pyridine is a very sensitive reagent for the detection of traces of phosphoric acid; it will detect 0·01 mg. of P_2O_5 in 10 c.c. of solution, whilst the limit for molybdic acid solution containing nitric acid is about 0·1 mg. of P_2O_5 in 10 c.c. The phosphoric acid in superphosphate can also be precipitated as a basic mercury compound by means of yellow mercuric oxide; this compound is then decomposed with sodium sulphide, and the phosphoric acid precipitated as ammonium magnesium phosphate. Precipitation as calcium triphosphate is untrustworthy. [See also *Ind.*, 160A.]

W. P. S.

Use of Textile Fibres in Microscopic Qualitative Chemical Analysis. II. Detection of Boron by means of Turmeric Viscose Silk Fibres. III. Detection of the Heavy Metals by means of Zinc Sulphide Wool Fibres. E. M. CHAMOT and H. I. COLE (*J. Ind. Eng. Chem.*, 1918, **10**, 48—50. Compare A., 1917, ii, 576).—Viscose silk fibres dyed with turmeric are

useful for the detection of very small quantities of boric acid; a reaction may be obtained with one drop of solution containing 0·000025 mg. of boron. Wool fibres, free from fat and treated with sodium sulphide and zinc acetate, are suitable for the detection of heavy metals, the coloration obtained indicating the metal present. [See, further, *Ind.*, 75A.]   W. P. S.

Rapid Organic Combustion. P. A. LEVENE and F. W. BIEBER (*J. Amer. Chem. Soc.*, 1918, **40**, 460—462).—The procedure adopted in the authors' laboratory is fully described, with diagrams. Cerium dioxide is used as a catalyst, and from the first weighings to the final ones, the combustion requires only about forty-five minutes.   J. C. W.

Micro-analysis of Organic Substances. J. V. DUBSKY (*Ber.*, 1917, **50**, 1709 –1713).—An account of recent experiences and improvements of micro-methods of combustion, made in the university laboratory at Zurich, where all analyses are now performed with small quantities of material. For the combustion of halogeno-nitro-compounds, the tube contains a 5 cm. layer of pieces of fine silver wire, then a 16 cm. layer of a mixture of copper oxide and lead chromate, then another short layer of silver, and finally the boat. The preliminary decomposition is carried out with the oxygen supply cut off, and if the compound is very poor in hydrogen (for example, trichlorodinitrobenzene) it is found best to adopt Benedict's method (A., 1900, ii, 439) and place before the boat another boat containing a weighed amount of pure benzoic acid, naphthalene, or sugar, in order to reduce some of the copper oxide. [See also *Ind.*, April.]   J. C. W.

Electrical Combustion Furnaces for Micro-analyses. J. V. DUBSKY (*Ber.*, 1917, **50**, 1713—1717).—A description of a platinum resistance and a chromium–nickel resistance furnace designed at the author's instigation for use with silica combustion tubes. [See *Ind.*, April.]   J. C. W.

The Eggertz Test for Combined Carbon in Steel. J. H. WHITELEY (*Iron Steel Inst. Carnegie Schol. Mem.*, 1917, **8**, 1—101).—Small quantities of carbon dioxide may be accurately estimated by absorbing in an ammoniacal solution of barium chloride (McFarlane and Gregory, A., 1906, ii, 802), and an apparatus is described by the use of which the carbon in steel may be estimated by wet combustion or the weight of carbon dioxide evolved during the Eggertz colour test may be determined. This gas is given off, at a decreasing rate, during several hours' heating, and the quantity obtained in a given time is closely proportional to the carbon content of the steel, irrespective of its heat treatment, the only exceptions being austenitic steels. The other volatile products of the reaction include hydrogen cyanide and hydrocarbons, the 'missing' carbon remaining in solution, as shown by oxidation with permanganate. A 1% carbon steel yields, in the

first ten minutes' boiling with nitric acid, 22% of its carbon as carbon dioxide, 5—10% as hydrogen cyanide, and 2—3% as hydrocarbons.

The colouring matter of the brown solution is colloidal. When steel is dissolved in nitric acid kept cool by water, a black precipitate forms in all cases in which carbide particles are visible in the section etched with sodium picrate. This precipitate becomes brown later, especially on warming, and later this changes to a brown solution. The particles first formed have the form of the carbide. Quenched steels yield the solution directly. On dialysis, a substance passes through the membrane, which has an orange colour in concentrated solution, but becomes green on dilution. The colour is not merely that of the organic substances present, but depends on the reaction of these with iron. With further heating, the green substance changes to a colourless or only slightly coloured substance. The proportions of the coloured products depend on the electro-chemical conditions of solution, and cold-worked steels give a deeper colour. The tints given by different steels are more easily matched if sulphuric acid be added. For 0·5 gram of steel, 10 c.c. of nitric acid (1·2) are used, and, after boiling for fifteen minutes, 15 c.c. of sulphuric acid (1 : 3 by volume) are added. [See, further, *Ind.*, 1917, 1097.] C. H. D.

Gravimetric Estimation of Potassium by Sodium Cobaltinitrite. C. V. GAROLA and V. BRAUN (*Ann. Falsif.*, 1917, **10**, 572—575).—The reagent used consists of 28·6 grams of cobalt nitrate and 50 c.c. of glacial acetic acid dissolved in 500 c.c. of water, and 180 grams of sodium nitrite also dissolved in 500 c.c. of water; these two solutions are mixed twenty-four hours before use and then filtered. The mixed reagent keeps for a few days only. Twenty-five c.c. of the potassium salt solution (containing about 0·250 gram of potassium chloride and free from other bases except sodium) are treated in a stoppered flask with 25 c.c. of the reagent, and, after about eighteen hours, the precipitate is collected on an asbestos filter, washed with 10% acetic acid, then once with 95% alcohol, dried at 100°, and weighed. The precipitate contains 20·74% of K_2O. The method is trustworthy for the estimation of potassium in fertilisers, soils, wines, etc. Ammonium salts should be removed previously by ignition and other bases by treatment with sodium carbonate and filtration. [See also *Ind.*, 168A.] W. P. S.

Estimation of Potassium and Sodium as Chlorides through the use of the Refractometer. B. A. SHIPPY and G. H. BURROWS (*J. Amer. Chem. Soc.*, 1918, **40**, 185—187).—The refractive index at 25° of a 20% sodium chloride solution is 1·36829, whilst that of a 20% potassium chloride solution is 1·35992. If, therefore, the refractive index of a 20% solution of the mixed chlorides be determined, the approximate quantities of the two salts can be found by a simple calculation. [See also *Ind.*, 168A.] W. P. S.

A Proximate Method for the Estimation of Rubidium and Cæsium in Plant Ash. W. O. ROBINSON (*J. Ind. Eng. Chem.*, 1918, **10**, 50—51).—After removal of phosphoric acid, calcium, magnesium, etc., the mixed alkali chlorides are fractionally precipitated with platinum chloride. The potassium, rubidium, and cæsium platinichlorides are collected, reduced in hydrogen and the resulting chlorides treated with concentrated hydrochloric acid. The solution thus obtained, containing all of the rubidium and cæsium chlorides and a large amount of potassium chloride, is then compared spectroscopically with standard solutions containing known amounts of rubidium, cæsium, and potassium chlorides, and prepared under the conditions given. [See, further, *Ind.*, 76A.]   W. P. S.

Colloido-chemical Methods for Estimating the Hardness of Water. L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 149—155).—The surface tension of soap solutions is diminished considerably by addition of small amounts of alkali hydroxides, but the addition to such alkaline solutions of small amounts of calcium or magnesium salts increases the surface tension. These facts might form a basis for a method for determining the hardness of water.
     S. B. S.

Estimation of Zinc by Schaffner's Method. V. HASSREIDTER (*Zeitsch. anal. Chem.*, 1917, **56**, 506—509. Compare A., 1917, ii, 509).—In any of the modifications of this method, the precipitation of the iron (whether it be a single, double, or treble precipitation), should be carried out under conditions which will minimise the retention of zinc. It is advisable to make a comparison precipitation at the same time, using a definite quantity of iron and zinc. The iron precipitate should be tested for the presence of zinc. [See also *Ind.*, 168A.]   W. P. S.

Estimation of Zinc on Galvanised Iron. O. BAUER (*Stahl u. Eisen*, 1915. 734; from *Ann. Chim. .anal.*, 1918, **23**, 21).—A measured and weighed piece of the metallic sheet is treated with a solution containing 2 grams of sulphuric acid and 2 grams of arsenic trioxide per litre; this solution dissolves the zinc readily, but does not attack the iron. When evolution of hydrogen ceases, the remaining sheet of iron is removed from the solution, washed, dried, and re-weighed. This method can be used only with galvanised iron prepared electrolytically; when it is made by the hot dipping process, an iron–zinc alloy is formed between the layers of iron and zinc, and this alloy dissolves in the reagent. The presence of iron in the solution indicates that the galvanised iron had been made by the hot process.   W. P. S.

Estimation of Lead as Phosphate and its Separation from Antimony. G. VORTMANN and A. BADER (*Zeitsch. anal. Chem.*, 1917, **56**, 577—580).—The solution, containing about 0·5 gram of lead nitrate, is treated with 5 grams of tartaric acid, then rendered

slightly ammoniacal, heated at 80°, and 100 c.c. of 10% ammonium phosphate solution are added. The mixture is kept at 70—80° for sixteen hours, then cooled, the precipitate collected, washed with dilute ammonium nitrate solution, dried, ignited at a low temperature, and weighed. If antimony is present, the quantity of tartaric acid used is correspondingly increased; antimony is not precipitated under these conditions, and may be estimated as sulphide in the filtrate from the lead phosphate precipitate. The method yields trustworthy results and is useful for the analysis of "hardened" lead. W. P. S.

Separation of the Copper Group from the Arsenic Group, with Especial Reference to the Identification of Arsenic. M. CANNON SNEED (*J. Amer. Chem. Soc.*, 1918, **40**, 187—191).— The method depends on the solubility of mercury, arsenic, antimony, and tin sulphides in a solution prepared by saturating a 12% sodium hydroxide solution with hydrogen sulphide and adding to each litre 400 c.c. of 40% sodium hydroxide solution. Lead, bismuth, copper, and cadmium sulphides remain insoluble. The solution containing the soluble sulphides is treated with ammonium carbonate to precipitate the mercury; arsenic, antimony, and tin sulphides are precipitated by hydrochloric acid, and the antimony and tin sulphides are separated by solution in warm concentrated hydrochloric acid. The arsenic sulphide is dissolved in ammonia, oxidised with nitric acid, and the solution at 80° treated with an excess of ammonium molybdate. The latter yields a yellow precipitate with the arsenic, and will detect as little as 1 part of arsenic in 225,000 parts of water. [See, further, *Ind.*, April.] W. P. S.

New Methods for the Estimation of Copper, Zinc, Cadmium, Nickel, and Cobalt. ADOLPHE CARNOT (*Compt. rend.*, 1918, **166**, 245—251).—To a solution containing any one of these metals, sodium carbonate in slight excess is added in the cold until it is just alkaline. The precipitate formed is then redissolved by the addition of just sufficient ammonium hydroxide, or, in some cases, ammonium carbonate, and the liquid is boiled, usually for five minutes, until precipitation is complete. The precipitate is washed, dried and ignited, and weighed as the oxide, or reduced and weighed as the metal. If the amount of precipitate obtained is very small, it is dissolved in a little nitric acid, the solution evaporated to dryness with a little sulphuric acid, and the metal weighed in the form of its anhydrous sulphate. In every case, it is essential to ensure the absence of all ammonium salts prior to the precipitation with sodium carbonate. W. G.

New Separations of the Five Metals of the Group Soluble in Ammonia. ADOLPHE CARNOT (*Compt. rend.*, 1918, **166**, 329—333. Compare preceding abstract).—If copper and zinc are present together in solution, they are precipitated and weighed as their combined oxides (*loc. cit.*), and these are then heated in a current of hydrogen. The zinc volatilises as formed, and the

residual copper is weighed. With a mixture containing copper, nickel, and zinc, the copper is first precipitated from the boiling acid solution by the addition of sodium thiosulphate and weighed as its sulphide. From the filtrate, the nickel and zinc are precipitated and weighed as the mixed oxides, these being then reduced in hydrogen and the nickel weighed. For an alloy of zinc and cadmium, the metal is dissolved in nitric acid and the solution evaporated nearly to dryness, and then diluted to 150—200 c.c. Sodium carbonate is added until the liquid is alkaline, and then ammonium sesquicarbonate and a little ammonia, the liquid being heated to just below 100° until it no longer smells of ammonia. The cadmium carbonate is washed by decantation with ammonium carbonate solution until free from zinc, and then ignited and weighed as cadmium oxide. The zinc is estimated in the filtrate by Meunier's method (compare A., 1897, ii, 464).

Cobalt may be separated from nickel, when in solution with it, by precipitation with ammonium sulphide in the presence of an alkali oxalate. The nickel passes through in solution on filtering, and is precipitated from the filtrate as nickel sulphide by boiling it with acetic acid. This method also applies to the separation of copper and nickel if an alkali sulphide is used in place of ammonium sulphide.

By a combination of these methods, the five metals if present in solution together may be separated and estimated.   W. G.

The Examination of Mercury Fulminate and the Analysis of Mixtures for Percussion Caps. PAUL NICOLARDOT and JEAN BOUDET (*Compt. rend.*, 1918, **166**, 258—259).—Free mercury may be detected in the fulminate by shaking 1 gram of the latter with 100 c.c. of a 5% solution of ammonium thiosulphate. All the fulminate dissolves and leaves the mercury as a grey powder or in metallic globules, which can, if necessary, be weighed.

For the examination of detonating mixtures, the percussion caps are treated first in the cold for two hours, and then at 60° for one hour with yellow ammonium sulphide. The mercury fulminate is converted into mercury sulphide, which is filtered off along with any powdered glass present. To the filtrate, ammonium sulphite is added, and the antimony sulphide which separates is collected and weighed. In the filtrate, the alkali metals are estimated in the usual way. Any chlorate or nitrate in the mixture is extracted with cold water and estimated in the usual manner. Any copper present, owing to the attack of the metal of the caps, will come down with the antimony sulphide, and may be estimated electrolytically after calcining the sulphides and extracting them with nitric acid.   W. G.

Estimation of Manganese in Steel in the Presence of Chromium and Vanadium by Electrometric Titration. G. L. KELLEY, M. G. SPENCER, C. B. ILLINGWORTH, and T. GRAY (*J. Ind. Eng. Chem.*, 1918, **10**, 19—23).—The manganese is

oxidised to permanganate by sodium bismuthate or ammonium persulphate, and the permanganate then titrated with mercurous nitrate solution. The solution to be titrated should contain about 50 c.c. of sulphuric acid (D 1·58) per 200 c.c. of water, and the temperature should be 20°. The end-point of the titration, as observed on the electrometric apparatus, is sharp and is not affected by the presence of chromates or vanadates. [See, further, *Ind.*, 92A.]   W. P. S.

Analysis of Tin Ores. T. F. GOLICK (*Eng. Min. J.*, 1916, 827; from *Ann. Chim. anal.*, 1917, **22**, 248).—The ore is fused with a mixture of potassium carbonate and sulphur, the mass, when cold, is extracted with hot water, and the solution filtered. The filtrate is then evaporated with the addition of sulphuric acid and heated until sulphuric acid fumes are evolved, the residue treated with hydrochloric acid and hydrogen peroxide to insure complete conversion of the tin into stannic chloride, and the tin precipitated as sulphide. After the precipitated sulphide has been collected and washed, it is treated with a known quantity of potassium iodate in the presence of concentrated hydrochloric acid, and the excess is titrated with potassium iodide solution; the reaction proceeds according to the equation: $SnS_2 + KIO_3 + 6HCl = SnCl_4 + S_2 + KCl + ICl + 3H_2O$.   W. P. S.

Detection of Small Quantities of Vanadium in Water. VICTOR L. MEAURIO (*Anal. Soc. Quim. Argentina*, 1917, **5**, 185—189).—A solution of 0·2 gram of diphenylamine in 100 c.c. of water in presence of hydrochloric acid gives a violet coloration with aqueous solutions of vanadium compounds. The coloration is unaffected by the presence of nitrates, iron, or titanates, and the test will detect the presence of vanadates in solutions of 0·0002% strength. [Compare *Ind.*, April.]   A. J. W.

The Estimation of Vanadium in the Presence of Molybdenum by means of Titanous Chloride. A. TRAVERS (*Compt. rend.*, 1918, **166**, 289—290. Compare A., 1917, ii, 545).—In using the method previously described (*loc. cit.*), it is now noted that if the indicator, potassium thiocyanate, is added before the titanous chloride, the vanadic acid is reduced first, and when this action is complete, the molybdic acid is reduced. Thus vanadium and molybdenum in steels may be estimated by carrying out the method for the two together, as already described (*loc. cit.*), and then in another portion estimating the vanadium alone by adding the thiocyanate first and running in the titanous chloride from a burette until an end-point is reached.   W. G.

Antimony Dioxide. JULIUS VON SZILÀGYI (*Zeitsch. anal. Chem.*, 1918, **57**, 23—28).—Antimony dioxide may be prepared by heating the pentoxide at bright redness or by oxidising antimony with concentrated nitric acid and heating the resulting oxide at dull redness until constant in weight. When heated with concentrated

hydrochloric acid and potassium iodide, antimony dioxide liberates iodine; the reaction proceeds according to the equation: $2SbO_2 + 6HCl + 2HI = 2SbCl_3 + 4H_2O + I_2$. The iodine may be separated by distilling the mixture; if the distillate is collected in a receiver containing potassium iodide solution, titration with thiosulphate solution will give the quantity of antimony dioxide present. Meta-stannic acid does not liberate iodine from potassium iodide under the above conditions, but the reaction is of little practical use for the estimation of antimony in·the presence of tin, since alloys of these two metals usually contain other metals which interfere.

<div align="right">W. P. S.</div>

Colorimetric Estimation of Bismuth (in Copper). H. A. B. MOTHERWELL (*Eng. and Min. J.*, 1917, **104**, 1091—1092; from *J. Soc. Chem. Ind.*, 1918, **37**, 92A).—The copper is dissolved in nitric acid, and the cold diluted solution treated with sodium carbonate until a small quantity of the copper is precipitated; this precipitate will also contain all the bismuth. After six hours, the precipitate is collected, dissolved in hydrochloric acid, the copper and bismuth are separated as sulphides, and these are dissolved in nitric acid. To the solution are added 5 c.c. of lead nitrate solution (13·5 grams per litre), the mixture is nearly neutralised with ammonia, treated with an excess of ammonium carbonate, boiled, cooled, the precipitate collected and dissolved in nitric acid, and the precipitation is repeated. If much copper is still present, dilute potassium cyanide solution must be added until the coloration has nearly disappeared, and the precipitate is then washed until free from copper. The precipitate is dissolved in a small quantity of nitric acid, the solution evaporated, the residue dissolved in three drops of nitric acid and 5 c.c. of water, the solution diluted to 25 c.c., and made up to 50 c.c. with 1·7% potassium iodide solution. The coloration obtained is at once compared with that given by a known amount of bismuth under the same conditions and in the presence of 5 c.c. of the lead nitrate solution.

<div align="right">W. P. S.</div>

The Estimation of Humus by means of a Simplified Procedure of Elementary Analysis. A. JAKOBSEN (*Zhur. Optyn. Agron.*, 1916, **17**, 93—98; *Expt. Stat. Rec.*, **36**, 614; from *Physiol. Abstr.*, 1918, **2**, 629—630).—The humus in soils is estimated by a combustion method, using platinised asbestos as a catalyst. From 1 to 25 grams of material may be used, and the oxidation is complete in thirty minutes. It is claimed that the method is as satisfactory as the more complex one of Gustavson.

<div align="right">W. G.</div>

Determination of the Concentration of the Hydrogen Ions in Acid Liquids. Application to Wines. MARCEL DUBOUX (*J. Chim. Phys.*, 1917, **15**, 473—501).—Two methods are described, namely, a graphic method and a method of calculation, the latter giving the more precise results.

In the first method, a neutralisation curve is drawn, plotting the conductivity of the solution against the volume of standard alkali added, the wine being previously diluted with water in the proportion of 1:4 or 3:97 by volume, according as the amount of alkali required to neutralise 1 litre of it, as determined volumetrically, is less or greater than 110 c.c. N-sodium hydroxide. The tangent to the curve at the neutralisation point is drawn, and the distance x from its point of intersection with the ordinate axis (conductivity) to the curve along the axis is measured. Then $[H^{\cdot}] = x/0\cdot291$, or $x/0\cdot157$, according to the dilution used.

In the method of calculation, it is necessary to determine (1) the volume of N-sodium hydroxide required to neutralise 5—5·2 c.c. of the wine; (2) the percentage of alcohol by volume in a mixture of 1 c.c. of wine to 4 c.c. of water; (3) the specific conductivity of the wine before and after the addition of the volume of alkali as determined in (1). Formulæ are given for the calculation of the hydrogen ion concentration from these data. W. G.

Volumetric Estimation of Formic Acid in the Presence of Hydroxides, Carbonates, Oxalates, and Acetates. F. TSIRO-PINAS (*J. Ind. Eng. Chem.*, 1917, **9**, 1110—1111).

—The solution, containing from 2·5 to 5 grams of formic acid, together with carbonates, oxalates, and acetates, is boiled for a few minutes, rendered alkaline with sodium hydroxide, and treated with a quantity of calcium chloride sufficient to precipitate the carbonates and oxalates. The mixture is filtered, the filtrate diluted to 250 c.c., and 50 c.c. are acidified with sulphuric acid and boiled in a flask with 400 c.c. of chromic acid solution (50 grams of sodium dichromate, 80 c.c. of concentrated sulphuric acid, and 500 c.c. of water) for fifteen minutes, the flask being connected, through a reflux apparatus, with a gas-measuring tube filled with water. When carbon dioxide ceases to collect in the measuring tube, the volume of the gas is observed, and its weight calculated into formic acid. Acetates, if present, do not interfere, as they are not oxidised by chromic acid. With pure sodium formate, the method yields 99·6% of the formic acid present. W. P. S.

Estimation of Acetic, Propionic, and Butyric Acids. R. D. CROWELL (*J. Amer. Chem. Soc.*, 1918, **40**, 453—460).

—Various principles underlying possible methods for separating the lower aliphatic acids are discussed, and a procedure is described which depends essentially on the fact that most of the butyric acid and some propionic acid can be extracted by means of light petroleum (b. p. 150—300°) after saturating the solution under examination with calcium chloride and a little potassium chloride. The total acidity and weight of sodium salts, dried at 200°, are first determined, and then the acidity and salt weight of the light petroleum extract. The first salt weight minus the sodium acetate equivalent gives the total weight of –CH₂ groups, and the second minus the sodium propionate equivalent gives the weight of –CH₂ groups present as butyric acid. A correction for the solubility of

butyric acid in the calcium chloride solution, etc., also requires to be made. [See, further, *Ind.*, April.]   J. C. W.

Detection and Estimation of Butyric Acid. G. DENIGÈS (*Ann. Chim. anal.*, 1918, **23**, 27—31).—Five c.c. of a butyric acid solution are mixed with 5 c.c. of hydrogen peroxide solution (0·01 vol. for each 0·01 gram of butyric acid per litre) and 1 c.c. of ammonium ferrous sulphate solution (5 grams of ammonium ferrous sulphate and 10 c.c. of 10% sulphuric acid per 100 c.c.). The mixture is heated at 70° for five minutes, then treated with six drops of sodium hydroxide solution, cooled, filtered, and 5 c.c. of the filtrate are mixed with three drops of sodium hydroxide solution, three drops of 5% sodium nitroprusside solution, and a slight excess (0·5 c.c. or more) of acetic acid. A red coloration develops, its intensity depending on the quantity of butyric acid present. The amount of the acid in the solution may be estimated colorimetrically by comparison with standards under the same conditions. The method may be applied to the estimation of butyric acid in mixtures, organic fluids, etc., after the acid has been separated by distillation or extraction.   W. P. S.

Estimation of Lactic Acid in the Presence of other Organic Acids. P. SZEBERÉNYI (*Zeitsch. anal. Chem.*, 1917, **56**, 505—506).—Lactic acid, when heated with chromium trioxide and sulphuric acid, yields acetic acid, carbon dioxide, and water; if the oxidised mixture is then distilled, the quantity of acetic acid in the distillate is a measure of the lactic acid present. The results obtained are slightly too low, since about 3% of the lactic acid is converted directly into carbon dioxide and water. Under the above conditions, tartaric acid, malic acid, citric acid, and oxalic acid are oxidised directly to carbon dioxide. Volatile acids, alcohol, acetone, and esters must be removed previously by distillation. A small portion of the lactic acid also distils over, and this quantity may be estimated approximately from the acidity and the molecular weights of the acids in the distillate. [See also *Ind.*, 165A.]   W. P. S.

Detection and Estimation of Small Quantities of Hydrocyanic Acid. J. M. KOLTHOFF (*Zeitsch. anal. Chem.*, 1918, **57**, 1—15).—Of the various reactions used for the detection of hydrocyanic acid, that depending on the formation of ferrocyanide is the only one which is characteristic and trustworthy. In using this reaction for the colorimetric estimation of small quantities of hydrocyanic acid, it is important to have exactly the same quantities of reagents in both the test and comparison solutions. The thiocyanate reaction (compare A., 1916, ii, 455) may be used for the purpose if it is remembered that certain body fluids (saliva, stomach contents, etc.) may already contain thiocyanate; in such cases, the hydrocyanic acid may be separated by the aeration-distillation method. The picric acid, guaiacum, phenolphthalein, silver, and iodine–starch reactions are untrustworthy, since many

substances other than hydrocyanic acid give similar reactions. In dealing with pure hydrocyanic acid, the sensitiveness of the tests (expressed in mg. of CN per litre) is as follows: ferrocyanide, 2; thiocyanate, 0·1; picric acid, 1; guaiacum, 0·004; phenolphthalein, 0·05; silver, 0·03; iodine–starch, 0·1. W. P. S.

Detection of Picric Acid by Ferrous Tartrate Reagent. RUPEAU (*Ann. Chim. anal.*, 1918, **23**, 15—16).—The author claims to have been the first to use ferrous sulphate–tartaric acid solution, often called Le Mithouard's reagent, for the detection of picric acid (compare A., 1917, ii, 158). W. P. S.

Detection of the Poisons which can be Extracted with Ether from the Acid Aqueous Solution in the Stas-Otto Process (Picric Acid, Picrotoxin, Antipyrin). O. TUNMANN (*Apoth. Zeit.*, 1917, **32**, 441—443, 447—448; from *Chem. Zentr.*, 1917, ii, 499—501. Compare A., 1917, ii, 551).—This is a continuation of the papers referred to. *Picric acid.*—The sublimates are homogeneous, colourless, or even yellow. Typical crystals cannot be reckoned on even after recrystallisation from water or alcohol. Hydriodic acid dissolves the sublimate at once, but no crystals are formed. Zinc chloroiodide dissolves rich sublimates only on warming; on cooling, large, yellow prisms and flat, prismatic crystals are deposited; they show strong pleochroism and extinction parallel to the long axis. Bromine–potassium bromide solution acts similarly, but the prisms are less regular and not pleochroic. On the whole, reactions like the *iso*purpuric acid reaction, the picramic acid reaction, and the dyeing of wool are most satisfactory for these microchemical purposes.

Picrotoxin.—The picrotoxin sublimes at 215—225° for the most part. The sublimate exhibits no crystals, but only drops, and crystallisation could not be brought about. Zinc chloroiodide and hydriodic acid yield no reaction products. Nitric acid dissolves the sublimate, but produces no coloration. Rich sublimates yield good crystals of picrotoxin when treated with hydrochloric acid, but it is better to apply 5% ferric chloride solution for this purpose, because this distinguishes picrotoxin sublimates from those of antipyrin. The sublimate and the solution are heated under a cover glass until bubbles appear; on cooling, typical pentagonal tablets can be observed. They are colourless, the large ones polarise in variegated shades and show oblique extinction. If the sublimate under the cover glass is treated with a drop of bromine–potassium bromide solution and heated, colourless prisms of bromo-picrotoxinin are formed on cooling. These crystals are monoclinic, and can also be obtained by the action of bromine water.

Antipyrin.—The residues from the ethereal extraction of the acid solution yield only traces of antipyrin, because the greater quantity of this substance is extracted only when the solution is alkaline. The sublimates at first consist of drops, which eventually form groups of radially arranged, flat, prismatic crystals, which polarise strongly. These antipyrin deposits yield deep red drops

with hydrogen iodide, shining droplets with zinc chloroiodide, and droplets also with bromine–potassium bromide solution. The colour reactions ordinarily used are evident even with the smallest quantities without the aid of a microscope. Two antipyrin reactions which yield decisive crystalline precipitates are to be found in the formation of nitrosoantipyrin and ferripyrin respectively. In the former case, the sublimate is dissolved in a drop of water and treated successively with a drop of 10% sodium nitrite solution and a drop of acetic acid. The green solution deposits doubly refractive, dichroic crystals, or, if it is heated, long, yellow prisms. The ferripyrin reaction is carried out by heating the sublimate with a drop of 5% ferric chloride solution under a cover glass until bubbles are formed; on cooling, orange-yellow crystals are deposited, mostly 30—50 μ (sometimes 80 μ) long, which show yellow shades in polarised light. The reaction distinguishes antipyrin from salipyrin. In the case of salipyrin, the sublimate consists of groups of bent needles. Addition of ferric chloride produces a violet solution which remains on heating, and no crystals are deposited unless too high a temperature has been used for the sublimation. In this case, a mixture of crystals of ferripyrin and salicylic acid may be observed.   R. V. S.

Microchemistry of some Opium Alkaloids. L. VAN ITALLIE and J. VAN TOORENBURG (*Pharm. Weekblad*, 1918, **55**, 169—178). —An account of tests applicable to the alkaloids *pseudo*-morphine, protopine, tritopine, cryptopine, laudanine, laudanidine, and laudanosine. [See, further, *Ind.*, April.]   A. J. W.

Modification of the Ehrlich Indole Reaction in Bacterial Cultures. W. NOWICKI (*Wien. klin. Woch.*, 1917, **30**, 983; from *Chem. Zentr.*, 1917, ii, 498).—The culture, which should contain 8—10 c.c. of peptone water, is treated with 1 c.c. of Ehrlich's reagent and two drops of 40% formaldehyde solution. On shaking, a reddish-violet coloration appears, and by addition of alcohol the solution may be made suitable for colorimetric examination.

R. V. S.

Analysis of Blood and Urine. O. I. LEE (*St. Luke's Hosp. Med. and Surg. Rep.*, 1917, **4**; from *Physiol. Abstr.*, 1918, **2**, 587). —A mixture, prepared by adding three parts of amyl alcohol to seven parts of phenyl ether, is advocated for the prevention of foaming in analytical work. A colorimetric method for the estimation of iron in urine is described, the iron being precipitated with ammonium persulphate and ammonia, incinerated, and the ash moistened with potassium thiocyanate. The iron content of normal urine varies from 0·06 to 0·12%.

For the estimation of chlorine in blood, the proteins are coagulated by the addition of acetic acid and heating the mixture. After filtration, potassium alum and sodium carbonate are added, and the mixture is boiled and filtered, and the yellow filtrate is titrated with standard silver nitrate until a permanent red colour is obtained.   W. G.

JUST PUBLISHED.

With 25 Illustrations.   Octavo.   10/- net.

THE MANUFACTURE OF INTERMEDIATE PRODUCTS FOR DYES

By JOHN CANNELL CAIN, D.Sc. (Manchester)

Examiner in Coal-Tar Colouring Matters to the City and Guilds of London Institute.

EXTRACTS FROM THE PREFACE.

Nothing is more important in the present revival of the aniline dye industry in England and America than a knowledge of the literature dealing with the manufacture of intermediate products. It is of prime importance to the would-be manufacturer to have, in a convenient form, detailed information as to the preparation of the materials he proposes to make, so that he may be sure that he will not spend time and money in re-discovering, perhaps, some process that may have been already elaborately described in an obscure book or periodical.

It appeared to the author that a concise account of the literature dealing with the manufacture of intermediate products for dyes might therefore be of considerable use, and in this book he has endeavoured to present such an account in detail so as to render it unnecessary to refer to the original descriptions. It may perhaps be stated that he doubts whether any single library in England contains the whole of the literature consulted.

The aim has been to record the most recent or the most trustworthy method of manufacture of each substance in the same detail as in the original publication, to mention other processes or modifications, and to record essential scientific data, such as melting points, boiling points, densities, solubilities, etc.

In a few cases the author has supplemented published descriptions by his own experience, and in certain important instances (for example, phenylglycine and benzanthrone) practically all the published processes are given in full.

CONTENTS.

The Old and the New Mineralogy.

Hugo Müller Lecture, delivered before the Chemical Society on
April 18th, 1918.

By Sir HENRY ALEXANDER MIERS, F.R.S.

WHEN I was honoured by the Council of the Chemical Society with
the invitation to deliver the first Hugo Müller Lecture, I was in
some doubt whether I ought to accept it. The task it involves is
not easy for one who during the last ten years has by adminis-
trative duties been taken altogether away from scientific work and
who has not been able even to keep in touch with the rapidly
increasing literature either in chemistry or in mineralogy.

But when I thought of my old and close friendship with the man
in whose memory this lecture has been instituted, and the regard
which I feel for his family; when I reflected on the helpful part
that he played in strengthening the bond of union between
mineralogy and other sciences; and in particular when I remem-
bered the kindly interest with which he encouraged me in my
younger days, I felt that the invitation of the Council laid a duty
on me which I could scarcely refuse, however ill-qualified I may
be to fulfil it adequately.

The excellent obituary notice of Dr. Hugo Müller in the June
(1917) number of the Society's Journal sketches in clear outline
both the character and the scientific career of this singularly
modest and wide-minded man. All who knew him will feel that
in him they have lost not only a warm-hearted and sympathetic
friend, but also an adviser whose sound judgment and varied
knowledge were only equalled by the unselfishness with which he
placed them at the disposal of others.

There can, I think, be no more kindly or more useful action
than to help young people at the outset of their career to do the
work for which they are best fitted by training and inclination;
and I am able to speak as one who owed to him, at least to some
extent, an introduction to congenial work.

As Professor Armstrong has recorded in the obituary notice to
which I have referred, it was largely owing to Dr. Müller's instru-
mentality, when as President of this Society he was a member of
the Executive Committee of the Central Technical College, that
the teaching of crystallography was introduced into the Chemical
Department of the College.

That was really the first recognition in this country of crystallo-
graphy as an independent subject, and the first recognition of its

importance to chemical students. I only regret that the recognised position given to crystallography by Professor Armstrong's action has apparently been lost by his retirement.

I was invited by Professor Armstrong to undertake the work, and was thus given the opportunity of teaching a subject in the practice of which I was engaged by my daily occupation as assistant in the Mineral Department of the British Museum.

You will understand, then, that I am glad for this among other reasons to have this opportunity of offering a tribute to Dr. Müller's memory.

Hugo Müller's interest in minerals began in his boyhood, and was no doubt stimulated during his student days at Leipzig by the influence of Professor C. F. Naumann, whose lectures he attended. Indeed, Professor Armstrong tells us that his first intention was to devote himself to geology; and although in later life his professional energies became more and more absorbed by chemistry and its applications to the industry with which he was concerned, and his leisure hours by botany and gardening, yet he always maintained his interest in minerals and mineralogy, and his acquaintance with the literature of the subject. Indeed, from 1901 to 1904 he was President of the Mineralogical Society.

He was always a great admirer of fine mineral specimens, and left behind him a very complete and representative collection which has been presented by his widow and daughter to my old department in the University of Oxford.

It may seem singular that with so pronounced an affection for minerals Müller was much more concerned to devote his analytical skill to vegetable than to mineral products. When he retired from business he carried on researches into the chemical constitution of organic products, mostly of vegetable origin, and did not, as might have been expected, take up work on the minerals, in which he was so deeply interested. In fact, his published mineralogical work was actually confined to the early years between 1850 and 1860.

Whether he ever intended to do scientific work on his mineral collection I am unable to say; but had he done so on his retirement from business, it would have been in very different circumstances from those which prevailed fifty years earlier, especially as regards the attitude of mineralogists towards chemistry.

It has occurred to me that I may make the present occasion an opportunity for contrasting this attitude as it was in 1850 with what it was at the beginning of the twentieth century when Müller retired from business, and what it is at the present day.

The period of his student days in Leipzig seems to me to have been a very interesting and a very critical period in the history

of this science, which was then just beginning to recover from a dangerous disease.

To explain what I mean, let me recall the views which were held by many of the most influential mineralogists at, or shortly before, that date.

In the mineralogical world, full sway was then still exercised by the "natural (or natural history) system" of Werner, of Freiberg, which had been developed and elaborated by his successor Mohs.

According to this system, and here I am quoting the words of Mohs himself, "Mineralogy is the natural history of minerals," and "the natural-historical properties are those with which Nature has endowed the bodies which it produces, provided those properties as well as the bodies themselves remain unaltered during the examination." The only characters of minerals, according to this view, which are of fundamental importance, and which are therefore to be used for the purpose of discriminating between species and of classifying them, are the external or natural-history properties, such as specific gravity, lustre, hardness, colour, frangibility, and crystalline form. Clearly this definition entirely excludes the chemical properties. To quote again the actual words of Mohs: "Properties which can only be used during or after a change cannot be employed agreeably to the principles of Natural History and must therefore be excluded from mineralogy. Properties of this kind are the fusibility of minerals examined before the blowpipe; their solubility in acids; phosphorescence produced by heat; chemical analysis instituted to ascertain the quality or relative quantity of the component parts." "If a person intends to acquire solid information in mineralogy he should examine well-arranged collections."

These views served, no doubt, to stimulate collectors of minerals and directed a good deal of attention to the desirability of bringing together the best possible specimens, and of comparing the external characters so as to discover their relationships. But that the chemical properties should be completely ignored on principle seems now almost incredible, especially when we remember that Berzelius had already published in 1816 a chemical classification of minerals and had even claimed that mineralogy is really only a branch of chemistry. The authority of Berzelius was even greater than that of Werner or Mohs; yet their methods persisted for another generation at Freiburg, which, as a great mining centre, was also a great centre of instruction in mineralogy.

It was during Müller's student days that the revolt against their ideas took place.

To obtain a general survey of the successive changes in the history of the science, one cannot do better than refer to the successive editions of J. D. Dana's "System of Mineralogy," which first appeared in 1837, and of which the sixth edition (1892) was prepared by his son and successor, E. S. Dana. In the first and second editions Dana not only adopted the natural history system then in vogue, but even endeavoured to make it more precise by a Latin nomenclature; but in the third edition, published in 1850, he suddenly shook off the trammels of this system and adopted a chemical classification.

Nothing could better illustrate the change which came over the science in the middle of the nineteenth century than the preface to this edition. In it the author says: "The Science of Mineralogy has made rapid progress in the past six years; chemistry has opened to us a better knowledge of the nature and relation of compounds; and philosophy has thrown a new light upon the principles of classification. To change is always seeming fickleness. But not to change with the advance of Science is worse; it is persistence in error; and, therefore, notwithstanding the former adoption of what has been called the Natural History System, and the pledge to its support given by the author in supplying it with a Latin nomenclature, the whole system, its classes, orders, genera, and Latin names have been rejected. . . . The system has subserved its purpose in giving precision to the science and displaying many of the natural groupings which chemistry was slow to recognise. But there are errors in its very foundations which make it false to nature in its most essential points; and, in view of the character of these errors, we are willing it should be considered a relic of the past."

The year in which these words were written was the very year in which young Hugo Müller entered the University of Leipzig.

It must have required no small courage for a man in Dana's position to make such a recantation, but the benefit to the science was great. His "System" was becoming the standard book of reference for systematists. His rearrangement of species and adoption of a classification based on chemical constitution carried much weight.

It is not surprising that Hugo Müller as a student became interested in a science which was just at that time the focus of a discussion involving such fundamental issues, a science which in spite of its antiquity and importance had for thirty years, in Germany at least, endeavoured to close its doors against the chemist. It is fortunate that there were a few men like C. F. Rammelsberg and Gustav Rose who perceived the vital import-

ance of chemical composition in the study of minerals and exercised sufficient influence to counteract the dangerous authority of Mohs. Rammelsberg in 1847 published a volume of translations of the works of Berzelius bearing on the classification of minerals, and was devoting himself to their systematic analysis. I have already in a memorial lecture sufficiently described to this Society his contributions to the subject. It was his analytical work which really rendered possible a scientific classification. Gustav Rose in 1852 published his crystallo-chemical mineral system, which has served as the basis of all scientific classifications of minerals since that date. In the preface to that work he says: "It might appear that I have adopted a mixed principle in constructing this system: but this is not the case. For though I fully agree with the view of Berzelius that the system should only have regard to the nature of the elements combined, and the formulæ which express the composition, yet it must be borne in mind that the crystalline form is merely the expression of a definite composition, and in this way it is all the more certain a guide because in many, perhaps most, minerals we are still far from such a complete knowledge of the composition as is required by Nordenskiöld's system. The crystalline form tells us much more than the mere chemical formula; it tells us how the atoms are united, and this difference in the mode of union of the atoms often conditions the external differences of bodies even more than the actual differences between the atoms."

Dana, even when he originally adopted the natural system in preference to the chemical system, had expressed the hope that in time the two would prove to be identical: but the principle of isomorphism which was destined to effect this reconciliation seemed at that time to be only an obstacle.

For example, Whewell, in an essay on the classification of minerals, published in 1828, had pointed out how desirable it would be if some coincidence could be found in the chemical and mineralogical systems; but he argued that the then recently discovered property of isomorphism rendered a chemical classification impossible, since a mineral may be from the chemical point of view a mixture of an indefinite number of species.

In his "History of the Inductive Sciences," thirty years later, he still despairs of the attempts to reconcile the two systems, and says: "The combination of chemical, crystallographical, physical, and optical properties into some lofty generalisation is probably a triumph reserved for future and distant years."

The conflict between the two systems was to some extent prolonged by the fact that, even though the purely chemical system might be scientifically correct, it did not afford the means of prac-

tically distinguishing between mineral species except by long and elaborate analyses, and even these might fail, since different minerals may have what is apparently the same percentage composition; on the other hand, the external characters did enable the well-trained mineralogist to determine a species with rapidity and precision. It was perhaps natural, therefore, that Freiberg, the centre of training for miners and practical mineralogists, should espouse the system of Werner and Mohs.

Naumann, who had been professor at Freiberg before he came to Leipzig, may have been predisposed in favour of it, but he did himself adopt a system based on the chemical characters; for, as he said, "they represent the actual material, the substratum which is the basis of all morphological and physical phenomena, and which finds its scientific expression in the chemical formula." But he was even more of a crystallographer than a chemist, and emphasised the equal necessity of taking form as well as composition into account. His text-book, "Elements of Mineralogy," ran through five editions between 1846 and 1859, and exercised a far-reaching influence. In the later editions, his system was practically identical with that of Rose.

I have dwelt at some length on the controversy between the adherents of the two systems of classification, not only because it was a controversy which divided mineralogists into two schools of thought, even up to the time when Müller went to Leipzig, but also because a very important principle was at stake and because little is said about this in the histories of chemistry where the controversy is mentioned. It was not merely an academic question of classification or one of practical utility, neither was it a matter which only concerned mineralogists. It was really a question of mental attitude towards scientific problems.

At the beginning of the century there had been a somewhat similar struggle concerning the relative importance of chemistry and crystallography for mineralogists. This resulted from the great advances in crystallography made by the Abbé Haüy following on the great advances in chemistry made by Berzelius. But at that time there was no reaction of the sort represented later by Mohs and his school. Even Werner himself was not prejudiced like his successors. He attached the greatest importance to chemical composition in a system of classification, whatever exaggerated views he may have held concerning the value of external characters for the practical determination of mineral species.

The contrast between the attitude of Mohs and that of Haüy is evident to anyone who reads the introductions to their respective treatises on mineralogy.

In his zeal to confine the science within what he considered its proper bounds, Mohs endeavoured to dissociate it not only from chemistry, but from geology. "Natural History," he says, "considers the natural products as they are and not how they have been formed." And again: "It is a matter of the highest importance to keep the sciences perfectly distinct from each other and strictly within their respective limits."

Haüy, on the other hand, had recognised to the full the value of co-operation between all the sciences concerned, including not only chemistry, but also physics and geology.

The contention of Mohs and his school that it was unnecessary, or even improper, to apply chemistry to the study of minerals, seems to me to represent the most dangerous mental attitude which is possible for a scientific man.

We are apt to regret the growing specialisation in science, and to think that half a century ago it was almost impossible for a scientific worker to be much of a specialist. But surely the school of Mohs was guilty of the worst type of specialisation. The earlier workers in general were no narrow specialists, because the dividing lines between the sciences were not decisively laid down. To Haüy, or Mitscherlich, to Wollaston, Brewster, or Rose, each discovery was a new scientific problem, and they were not much concerned to decide whether to use the methods of physics or chemistry or geology for its solution.

Frontiers have always been the scenes of greatest activity, and it is precisely on the borderland between two sciences that the most fruitful progress has been made.

A man is not a specialist to the detriment of himself or his science, even though he devotes his whole life to the study of a single problem, provided that he makes sufficient excursions over the frontier in the interests of his life's work. But Mohs and his school endeavoured to isolate mineralogy (including crystallography), and to make it an independent science apart from chemistry, physics, and geology, instead of regarding it as a meeting ground of these sciences. The aloofness engendered by their action did great harm both to mineralogy and to chemistry; it tended to withdraw mineralogy and crystallography from the purview of chemistry, and it also closed the eyes of mineralogists to advances in chemistry that should have been of vital importance to them.

History repeats itself, and what has happened before may happen again. This lectureship will, I hope, always be one of the safeguards against exclusiveness and specialisation and will aid mineralogists and chemists to understand and help each other. If

it does this, it will perpetuate the spirit of the man whose name it bears.

The harm of this isolation extends to matters that appear to concern only systematic mineralogy, such as classification. After all, a classification which is right or wrong for minerals must be also right or wrong for other crystallised substances if it is based on what is essential; its merits or shortcomings would sooner or later be disclosed if the underlying principles were applied to other substances.

One regrettable result of the policy of isolation was that for a long period the study of minerals was divorced from that of organic or even of other inorganic substances, and that the study of crystallography was confined to mineralogists. This was partly, no doubt, due to the fact that minerals afford such splendid examples of crystallisation, and partly because a knowledge of the crystal properties is so useful in their practical identification.

Let me here finish with this subject of classifications and remind you that it was not until a later period that attempts were made to include all crystallised substances in a wider scientific survey and in a common study. Indeed, it is only within the last few years that a comprehensive catalogue of them all has been attempted by Groth in his "Chemical Crystallography," which began to appear in 1896, and is not yet completed.

During the same period, the Russian crystallographer Fedorov has been constructing a general table of crystalline substances so arranged that it is possible to identify any known substance by means of the characteristic angle of a single crystal when once it has been set up in the right position according to the rules which he has formulated. Mr. Barker has recently shown in a striking example the practical utility of this table even for the purposes of the medical man, by thus identifying a minute crystal of salol of intestinal origin (*Lancet*, May 26th, 1917).

That there should be several classifications made for different purposes within the same science is probably a quite wholesome principle: one may, for example, bring out constitutional relationships, and another be useful for determinative purposes.

But of far greater scientific importance than the systematic classification of minerals or the discovery of new methods for their identification is the question, What are the actual relations between the physical, geometrical, and chemical characters of a crystallised mineral? Only in proportion as this study has grown by co-operation with chemistry and physics did the science of mineralogy advance successfully along the path opened up by Haüy and

Berzelius, by Mitscherlich and Wollaston, by Rose and Rammels-
berg.

In this new purpose, and in the changed attitude of mind that
it involved, lies, I think, the essential difference between the old
and the new mineralogy which it is the object of this address to
emphasise, and it is time for me to turn to the later developments.

The newer mineralogy with this purpose in view has only made
progress by the employment of every available physical and
chemical method in the accurate study of carefully selected
specimens.

In the first instance, it was difficult to do much with isolated
species for lack of suitable experimental methods, such as have
been developed during the present century. Having ascertained
the exact chemical constitution, to determine with any reasonable
probability the actual arrangement of the atoms or molecules in
a crystal which may account for its form and physical characters
was too difficult a problem with the experimental resources then
available.

But the relations between different minerals belonging to the
same group in which it could be assumed that, whatever they
may actually be, the structures and constitution are similar, were
gradually worked out.

The laws of vicarious replacement of one element or radicle by
another were studied, and the variations of physical characters with
the change of chemical composition in many an isomorphous series
constituting a mineral group were successfully traced ; and it must
bo confessed that for these researches the foundations had not
infrequently been laid by the adherents of the natural history
methods, for they had recognised many minerals as belonging to
very definite mineral species and groups in spite of their chemical
differences.

It was understood, for instance, that the pyroxenes or the
felspars, whatever might be their percentage composition, do con-
stitute a group, and it was natural to conclude that the remark-
able similarity in physical properties shown by the various members
of the group must correspond to a mutual replacement of certain
elements or radicles, though the exact nature of these radicles might
be still doubtful. For example, the growing importance of petro-
graphy and the use of the polarising microscope led to a vast
amount of study being devoted to such minerals as the felspars, so
that it was not long before it became possible to determine with
accuracy by means of the microscope the exact chemical constitu-
tion of a minute crystal grain belonging to this group without
analysis.

Q*

On the other hand, it is still doubtful how the elements are actually associated with each other in the mineral, or what radicles are to be regarded as corresponding with each other in such isomorphous groups, mixtures, or solid solutions. To establish this sort of knowledge, a great deal of very careful chemical analysis was necessary, accompanied by an equally careful physical study of the specimens analysed. It was to work of this character that most of the important advances in chemical mineralogy during the second half of the nineteenth century are due.

I select as a conspicuous example of this type of research Penfield's investigation of topaz, to which a very definite chemical formula had been assigned, although it was known that the mineral exhibits some variations both in composition and in physical characters.

The most reasonable view seemed to be that the radicle AlO may be replaceable by the radicle AlF_2. The insignificant and variable traces of water were ignored. Careful analyses and accurate measurement of the angle between the optic axes, however, led Penfield to the conclusion that the optical characters vary regularly with the proportion of water, or rather of hydroxyl, and that the simple formula $Al_2F_2SiO_4$ is entirely satisfactory if it be understood that fluorine is replaceable by hydroxyl.

Many minerals and mineral groups have now been investigated with equal success: but almost every mineral contains an intermixture of various allied compounds as well as enclosures of other minerals, and therefore it is rather to the study of pure laboratory products that we have to look in the first instance for more precise knowledge concerning the relations between form, physical properties, and composition.

A vast number of isomorphous groups have now been studied in detail and with accuracy.

Tutton's classic investigation of the sulphates and selenates of potassium, rubidium, cæsium, and ammonium is one of the most conspicuous and complete examples. Others extending over the whole field of inorganic and organic compounds are recorded and discussed in Groth's "Chemical Crystallography."

I need only mention such studies as those of Jaeger on the benzene derivatives and the nitroanilines, of le Bel and Ries on the platinichlorides, of Jee, Rodd, Colegate, and others working with Armstrong on the benzene derivatives, and the investigations associated with the names of Gossner, Steinmetz, and others working with Groth at Munich.

All these advances in chemical crystallography have only been rendered possible by a vast amount of research on countless sub-

stances examined in the laboratory by a new generation of chemists who had acquired a knowledge of the methods of crystallography and an interest in its principles.

Although in these and similar investigations the exact morphological effects of the replacement of one element or radicle by another have been determined, I fear it cannot be claimed that the general laws of morphotropic action have been discovered even at the present day.

Now let me return for a moment to the year 1850. That year which, as I have indicated, was notable in the history of systematic mineralogy, was even more important in the history of crystallography, for it witnessed the publication of Bravais's memoir on the regular arrangement of points. This research first established a principle capable of explaining the homogeneity of crystals, their symmetry, the distribution of their faces, and their cleavage.

The mathematical treatment founded by him was elaborated by Sohncke and others, until finally and independently, towards the close of the nineteenth century, Schönflies, Fedorov, and Barlow determined and tabulated all the possible arrangements of material which can build up a homogeneous crystal, and so completed the pure geometry of the subject.

But when it came to the application of these geometrical principles to actual crystals and to the question what are the units which are arranged in this manner, it was the custom to fall back upon the assumption that these are "physical molecules" consisting of an unknown aggregate of "chemical molecules." Indeed, an attempt made by Sterry Hunt in 1891 to determine the degree of polymerisation from the specific gravity, hardness, and solubility led him to the conclusion that there are 584 chemical molecules in the physical molecule of calcite and 950 in that of quartz.

When speculation runs riot, it is a sign that experiment is needed. It is clear that there was need of new experimental methods to curb such wild views, and not only in this, but in other branches of mineralogy; for there were equally uncontrolled speculations concerning the origin of minerals, and especially rocks, and the processes by which they have solidified from solution or fusion.

It is in these later experimental methods that what I venture to call the new mineralogy distinguishes itself from the old mineralogy belonging to Müller's student days. And the change has mainly been rendered possible by recent advances in physics and chemistry, and particularly in physical chemistry.

There are two stages in the history of a crystallised mineral, that which terminates immediately before it solidifies and that

which begins at the moment of solidification. Both are of equal importance and interest to the mineralogist, and upon both a flood of new light has been thrown by recent investigation.

The excellent abstracts of the *Journal* of this Society and its "Annual Reports on the Progress of Chemistry" record all the important researches bearing on these problems. I need not do more, therefore, than select one or two conspicuous examples.

To deal first with the origin of minerals and the stages that preceded their crystallisation.

The application of the laws of physical chemistry, especially the recently discovered properties of solutions, found its most fruitful results in the studies of the Stassfurt deposits by van't Hoff and his pupils. There can be little doubt that we have now a well-established history of the manner in which these deposits have been laid down from solution and the nature of the solutions from which they have crystallised. Before these researches, there had been much speculation as to how such deposits might have originated from the evaporation of saline water, but it was only by the laboratory experiments begun by van't Hoff in 1897 and carried on through a series of years that the geological history of the deposits has been finally and fully reconstructed, including the order and conditions of deposit of more than thirty mineral species.

Nothing like this had previously been achieved. The processes previously invoked in explanation of the origin of minerals had been largely hypothetical, not experimental; with these researches, a new chapter in the history of mineralogy was opened.

It is unnecessary to refer to any details of the experiments. The excellent summary published by Dr. E. F. Armstrong in the British Association Report for 1901, and since that date the Annual Reports of this Society, have helped to make them widely known.

To take another example. It is of vital importance to the geologist that the history of rock formation should be deciphered, and for this purpose the newly established laws of physical chemistry were also directed to the problem of the crystallisation of the silicates.

Igneous rocks were for the first time regarded as solutions, and the physical properties of solutions were applied to the crystallisation of rocks from molten magmas. Vogt, in particular, endeavoured to show by his researches on slags, and with remarkable success, that they have crystallised in accordance with the laws of eutectic mixtures and of mixed crystals. A whole new field of research was thus opened up; but here again much of it was highly speculative until within the last few years the actual crystallisation of molten silicates has been brought within the range

of experimental study. Doelter, of Graz, and his pupils are responsible for much of this work, but more recently the experiments conducted at the Geophysical Laboratory at Washington have constituted a very remarkable advance.

The appeal to experiment has replaced a mass of speculations concerning theoretical solvents and the order of crystallisation, which were based only on field observations and bulk analyses. Now that sufficiently high temperatures can be attained, these investigations are of the greatest importance both to the geologist and to the mineralogist, since they reproduce in all probability the main conditions under which rocks have crystallised. One feels that for the first time the laws of their solidification are being traced and that they can be verified by experiment.

I need not do more than quote as examples the very full researches by Bowen and Anderson on the binary system magnesia and silica, and the ternary systems diopside–forsterite–silica and anorthite–forsterite–silica, and more recently by Bowen's investigations on diopside–albite-anorthite, and those by Rankine and Wright on the system lime–alumina–silica.

Such questions as the order of crystallisation and the actual position of eutectic mixtures in the process of solidification can now be determined by actual experiment, and not merely by the microscopical study of the solid rock. Not the least remarkable result of many of these experiments is the absence of the eutectic structure so characteristic of alloys, suggesting that perhaps too much importance may have been attributed to it by petrologists.

Some of this work has also thrown valuable light on the past history of rocks and minerals.

To quote only one example; direct experiments on the melting and inversion temperature of quartz have indicated that at 575°, within a very close approximation, it suffers enantiotropic change to the phase now recognised as β-quartz, and that above 800° quartz is no longer stable at ordinary temperatures, but becomes converted into tridymite. It is therefore suggested that quartz may be used as a geological thermometer serving to record the maximum temperature which has been reached by certain rocks. A similar use may perhaps be made of other minerals.

Such work as that of Bowen on the melting points of the felspars and their mixtures is of the highest value in tracing the past history of rocks and their minerals. His conclusion that albite and anorthite have the same molecular complexity in the liquid as in the solid state is one more stage in the simplification of our ideas concerning the constitution of minerals.

The pressure is, of course, an all-important factor which must

not be left out of account in speculations concerning the past history of rocks. Change of pressure may affect the order of crystallisation of the minerals which separate, and may determine their nature, as profoundly as change of temperature. Experiments at high temperatures combined with high pressure are now for the first time becoming possible with improved laboratory apparatus.

These experimental researches on the application of the law of solutions to minerals are not confined to silica and the silicates, but have already been extended at the geophysical laboratory to the copper sulphides and the oxides of iron. Experiment has yet to be applied successfully to such questions as magmatic differentiation, the effect of mineralising agents, pneumatolysis, and many similar problems. On the more vexed questions relating to the history of vein minerals and the large class of secondary deposits which line the cavities and fissures of the earth's crust, experiment will have much to say, though it may be a long time before experimental investigation on these subjects can be fully developed.

In the work of van't Hoff and in that of the Washington geophysicists, we have two conspicuous examples of what I mean by the new mineralogy as applied to the problem of the origin of minerals and rocks, that is, to the stage through which they pass up to the moment of solidification.

This application of experimental methods in which an attempt is made to realise the conditions of mineral growth replaces a vast amount of speculation with which the science was burdened during the last fifty years, and it unsettles some of the elaborate classifications, especially of rocks, which have occupied too much time and thought during the same period.

Surely classification as a means of arriving at general laws is an unsafe guide in the inorganic world if based to any large extent on hypotheses; it only serves to perpetuate them. Its proper function is to record the application of the general laws established by experiment, and any classification must inevitably change with new experimental results. For this reason, the attempts which are now being made by a group of American geologists to establish a natural classification of rocks with a new nomenclature are surely doomed to share the fate which befell the natural classification of minerals.

Let us turn next to those problems that concern the nature of minerals after they have solidified.

In this field also there had been an immense amount of speculation during the last half of the nineteenth century concerning the nature and arrangement of the units which constitute a crystal.

Somewhat surer ground was reached by the conception of topic axes introduced by Becke, and employed by Muthmann and Tutton, which gave suggestive evidence concerning the relative dispositions of the crystalline units along corresponding directions in a series of isomorphous substances, and indicated the increased or diminished separation of these units along a given direction when one element or radicle is replaced by another.

The importance of the molecular volume in these relations has been emphasised by Barker's experiments on the parallel growth of one substance on another; I have considerable faith in this as a sure experimental method which has yet to be used in tracing similarities of structure even where there is no chemical relationship.

. The crystallographic study of closely allied substances has further led directly to speculations concerning the relative positions of the *atoms* in the crystal structure, as, for example, in Muthmann's study of the perchlorates and permanganates, which was the first conducted from the point of view of topic axes; and, again, the relationships between the nitrates and carbonates led early to similar speculations concerning sodium nitrate and calcite.

To take another example in which this problem was attacked in a different way, Sollas endeavoured to ascertain the positions of the elements in sodium nitrate by comparing the specific refractive energy of the crystal in its two principal directions, and in the case of potassium copper chloride he combined this feature with the dichroism which he interpreted as indicating that the crystal is of a cuprous nature in one direction and of a cupric nature in another.

It is interesting to note that such speculations were already assuming that in most crystals the structural unit is probably an aggregate of not more than a few molecules, and in some perhaps the molecule itself. This was a great contrast to the earlier assumptions concerning polymerisation in the crystal molecule. Indeed, it was not long before expression was given to the extreme view that the structure is to be regarded as a regular arrangement of atoms in which the grouping into molecules is merely a geometrical fiction, whatever may have been their significance immediately before the act of crystallisation. This view was stated in a paper read by Professor Groth to the British Association as far back as 1904, in which, speaking of new ideas concerning crystal structure, he said, "it is unnecessary to assume the operation of any 'molecular forces' in addition to the forces which act upon the atoms themselves."

If, as I have said before, we are not yet in sight of the general

laws of morphotropic action even within groups of closely allied substances, we are still further from the supreme problem how from the chemical composition of a substance to deduce the form and physical properties of its crystal. The great test of a theory is the question whether it will enable us to predict, and in this sense there is as yet no satisfactory theory of the nature of a crystal. A bold and original attempt has been made by Pope and Barlow with some measure of success, and their theory of crystal structure which is based on the atom as the structural unit and endeavours to explain the form of the crystal from the atomic magnitudes, as indicated by the valencies, combined with the principle of close packing, has already inspired several very important investigations.

But in regard to the structure of the solid crystal, just as much as for the process of crystallisation to which I have already alluded, the need was for new experimental evidence—for some method of investigation which could explore the structure with a finer discrimination than that provided by the transmission of light or heat.

And now, as all the world knows, it seems that direct evidence concerning the arrangement of the parts of a crystal, the magnitude of the intervals between them, and even the spacing of the atoms, is supplied by X-ray methods, and in particular by the classic investigations of the Braggs.

In the history of crystallographic discoveries it has not infrequently happened that the crystal has first revealed some unknown physical phenomenon, has then supplied the mechanism or the material for studying it, and for establishing the principles by which it is governed; then, finally, these principles have been turned back upon the crystal in order to explain its nature. This was so with the phenomena of double refraction; calcite disclosed the new fact of double refraction to Bartholinus and Huygens, and this led to the discovery of the laws of propagation of light; these in turn were applied to the study of crystals, and have proved the most potent instrument that we possessed until lately for researches into crystalline structure. It was so again with circular polarisation and with pyroelectricity.

And so it is now with the new X-ray methods. The crystal reveals the new facts and then lays itself bare to attack from the physical weapon which it has forged. Indeed, in these remarkable investigations it is difficult to say which is the more valuable, the evidence which the crystal gives concerning the nature of the radiations or the evidence which the radiations give concerning the molecular or atomic intervals in the structure of the crystal.

If I do not dwell at length on these researches, it is not through any failure to recognise them as by far the most important advance of recent years, even in the science of mineralogy, but only because they are now so familiar to the scientific world. They have, of course, not destroyed anything that had been established by mathematical deduction from previous experimental evidence, but they have supplied new experimental methods of a most fundamental character for the study of crystals.

The assumption on which Bragg's interpretation is based, namely, that the crystal consists of material distributed in equally spaced plane layers or in layers separated by intervals which recur regularly, corresponds with all that had been laid down by purely geometrical considerations, and it has been confirmed by all that we know about the physical properties of crystals.

Indeed, if it were needed, evidence of the existence of plane internal layers parallel to possible faces of the crystal is supplied by the X-ray analysis. For Canac and others have shown that it is possible to measure the angles of a crystal by X-ray reflections from the internal planes just as certainly and almost as accurately as by the reflection of light from the external faces of the crystal.

The care which must be exercised in the interpretation of X-ray measurements in their present early development is illustrated by Vegard's observations on the rutile group of minerals, in which a structure based on the reflections observed by him has been subsequently shown to be erroneous, because certain intermediate reflections were overlooked.

Whether the X-ray analysis can supply evidence as to the existence or nature of the chemical molecule in the crystal is a more difficult question into which I do not feel competent to enter.

In crystallographic research I have nothing to record quite corresponding with the work of the Washington geophysicists, for the simple reason that there is for crystallography no department corresponding with the geophysical laboratory.

In my opinion, the importance of the study of crystals has now become so great, not only for the identification of substances by crystal measurement, but also on account of the new knowledge which modern crystal study is contributing to problems belonging to different sciences, that there is real need for a department of pure crystallographic research, one in which such studies can be carried out quite independently of elementary teaching or of immediate applications, and without being tied to mineralogy. I venture to hope that it will not be long before some such department is founded either in connexion with one of our universities or elsewhere.

There is yet another notable field of work in which the later physical discoveries have opened up new experimental methods in mineralogy. The past history of minerals may now be discussed in the light of their radioactivity, and the study of radioactive changes is giving some indication of a process of progressive change, if not in the minerals themselves at least in the elements which they contain. For the first time, therefore, speculations concerning the age of certain minerals can be based on direct experimental evidence.

The remarkable pleochroic haloes which surround zircon and other radioactive minerals enclosed as microscopic crystals in mica, cordierite, and other rock-forming minerals, were investigated by Joly from this point of view; and in the hands of Strutt, Boltwood, and others the proportions of uranium, radium, thorium, helium, and lead in radioactive minerals have been made an instrument not only for exploring the history of the disintegration changes in these elements, but for estimating the actual age of the minerals. A new importance now attaches to the accurate analysis of such minerals in respect of rare elements which previously escaped notice, and also to the choice of the specimens analysed, for, as Boltwood points out, it is necessary to distinguish between the more ancient primary minerals and those of secondary, and therefore of more recent, origin.

From the mineralogist's point of view, we have passed out of the stage in which the object is to ascertain the formula and to study the mutual replacements of elements and radicles in order to classify minerals into definite species, and have begun to study the mode of association of the elements and radicles within the mineral, both now and during its past history.

In selecting only three or four conspicuous examples of the progress of mineral chemistry during the last fifty years, I have, of course, passed by without notice many very remarkable advances made in other branches of the subject, such as analytical methods and interpretation of analyses, the synthesis of individual minerals, the alterations, replacements, and transformation of minerals both in nature and in the laboratory, the improvements in apparatus for the accurate measurement of physical constants, new methods of separation, the introduction of microchemical analysis, the relations between colour and radioactivity, and a host of other advances.

I have also omitted specific mention of all the recent work on the constitution of the natural silicates, and this for a reason which I must state.

The history of modern views concerning this, the most important

group of minerals (constituting with silica about 90 per cent. of the earth's crust), begins, not long after the period to which I have confined my survey, in 1864 with Tschermak's discovery of the nature of the felspar group as mixtures of albite and anorthite. This led the way to attempts to explain the analyses of many other complicated silicates as mixtures of compounds not so similar to one another as those which had previously been classed as isomorphous, and in some instances far more dissimilar than albite and anorthite.

When, however, such minerals as the pyroxenes, amphiboles, mica, and tourmaline were discussed, the analyses could only be interpreted on this principle by the aid of a host of possible silicates which are not known to exist; and although some experimental guidance in these speculations has been supplied by the work of Tschermak, Schneider, Thugutt, and others on the acids which could be isolated or the residues which could be obtained by decomposition of the mineral, yet the interpretation of the analyses remained to a large extent hypothetical.

The evidence supplied by pseudomorphs, which show the initial and final products in the case of an altered mineral, cannot give any sure information about the solvents which have acted or the intermediate minerals which may have been produced during the process of change. Even experiments on the decomposition of silicates only in general produce compounds which are stable, and lose sight of compounds, unstable in themselves, which may enter into the constitution of the mineral. In the pyroxene group, for instance, synthetical experiments indicate that the diopside molecule may form a solid solution with several unstable silicates, as well as with alumina or ferric oxide, so that Rammelsberg's view of the group as a mixture of the diopside molecule with alumina is not necessarily more unreasonable than Tschermak's more usually accepted interpretation founded on the analogy of the felspars.

And if we make a general survey of the views which have been expressed on the constitution of the silicates, and especially of the alumosilicates, including Vernadsky's theory of the chlorite nucleus and the mica nucleus, and the more recent and attractive hexite–pentite theory of W. and D. Asch, we have to confess that we are still waiting for more experimental evidence before we can be on sure ground. In so far as these theories suggest new experiments, they perform a most valuable function, but they are not to be regarded as in any way equivalent to experimental results.

Synthetical work such as that of Clarke, Lemberg, and Doelter; the discrimination of solid solutions from double salts by careful melting-point determinations; study of the properties of pure

artificial silicates, their combinations and disintegrations; the manufacture of additive compounds and derivatives; the study of such replacements as those of water by alcohol, benzene, and other substances in the zeolites investigated by Friedel, and the adsorption experiments of Grandjean—these are examples of the sort of researches which must be largely extended before constitutional or structural formulæ can be assigned with any confidence to the silicates, and especially to the alumosilicates.

For the present, the freedom of speculation which is possible concerning the chemical structure of minerals bears some resemblance to the unchecked freedom with which the physical and geometrical structures were handled before the advent of X-ray methods and the unrestrained speculations on the crystallisation of magmas and mineral solutions which prevailed before the experimental methods of physical chemistry were applied. We still await the key of experiment which may unlock the secret of the chemical constitution of the silicon compounds.

For this reason, without desiring to ignore their interest and importance, I pass over the whole subject of modern theories concerning the chemical structure of the silicates.

Let me, finally, ask the question: In what fundamental respects does the new mineralogy differ from the old of fifty years ago, and what are the prospects for the future? Is it anything more than the pursuit by new methods of the old problems? A more refined study than was possible then of the characters and properties of minerals? And the answer, I think, is that it is a great deal more than this, for the whole purpose of the quest has changed. Our object is no longer merely to trace the relations between different minerals, neither is it our purpose to classify them as animals and plants are classified in order to ascertain the laws that govern these relations. The importance of such classification and study of characters in the biological sciences is due to the fact that the record is one of constant change and development: the careful definition and study of species leads to the laws of evolution. In the mineral kingdom there is apparently no such prospect. Our main purpose is now not to discover how one mineral has been evolved from another, for there is no such evolution, or even how it is related to others, but how it has been constructed from its constituents. We are concerned with the question how its elements came together, and how they are united to form the mineral; and why among the elements that build up the earth's crust only certain combinations occur as minerals, whereas millions of combinations are theoretically possible. The wonder is not that there are so many minerals, but that there are so few; that mineral

species, for example, are so vastly outnumbered by the species of insects.

So long as the crystal unit was supposed to be an unknown multiple of the chemical molecule, these problems seemed far from solution, but now that we appear to be better justified in dealing, not so much with the arrangement of molecules as with the arrangement of atoms in the crystalline structure, one cannot help feeling that the structure must be one of greater simplicity than the complicated silicate formulæ seem to indicate. We may surely hope that minerals will prove to be comparatively simple groupings of the elements, that the discovery of the laws which determine the limited number of minerals existing as stable substances will lead us to a clarified vision of the conditions which determine equilibrium in non-living matter on the earth's surface, and that we may expect an answer to the question why the elements have come together and how they are united to form the beautiful compounds which constitute the mineral kingdom.

This change in the scientific prospects of mineralogy is due to the advent of new experimental methods and principles. The promise of a revived interest and an increased progress in this science lies in the application to minerals of every new experimental treatment, physical or chemical, that can be employed.

In this, as in many other sciences, far too much energy has been expended in the past on the repetition and refinement of old investigations, on the mere improvement of old methods of research or of apparatus, on questions of nomenclature or description. Although I do not wish to underestimate the value of accurate data patiently accumulated by prolonged and careful research, without which no sound foundations can be laid, yet I feel that for long periods mineralogy stagnated because time and energy were occupied in compiling interminable lists of uncertain crystal faces or in the analysis of impure specimens.

The real advance takes place when new methods of attack are turned upon the old subjects.

The physical properties of solutions, X-ray analysis, and radioactive changes are the three examples which I have quoted; they have infused new life into the science; but they are only three, and will have to be multiplied indefinitely.

Minerals deserve all the study that they can get; they supply the most perfect and the most varied materials; almost every known element is contained in them; they are extraordinarily stable compounds; they teem with problems, owing to the variety of conditions under which they exist or have been formed.

Especially would I attach importance to the fact, too often for-

gotten, that mineralogy is one of the natural history sciences, and therefore deals with natural objects not only as we find them in museums, but investigates their relations and their past history; while it studies their properties by applying to them all the known resources of the laboratory, it also studies through them the operation of the laws of nature, both now and in the distant ages of the past. In mineralogy, as in botany and zoology, it is in general impossible to reproduce past conditions; they have gone for ever. But there is this great difference between mineralogy and the biological sciences. Whilst they trace the history of changing species in the light of modern experiments and observations, the only record of their past, and that a secondary and an imperfect one, is supplied by fossils: the organisms themselves have disappeared.

On the other hand, in the case of crystallised minerals, we generally have the actual object surviving through the ages. The liquid carbon dioxide imprisoned in a quartz crystal, or the tiny zircon surrounded by its halo in mica, have been there for untold centuries and survive to tell the tale of their own history. The same is true of the radioactive mineral, which by its present composition gives a clue to past changes; the structure of the crystal remains as a permanent record of its original nature. We have in our hands the very object that existed millions of years ago, and not merely a cast of it, and we can continue on it the processes that nature has begun. The forces of crystallisation that brought together its component elements have held them together in the same relative positions, of which the unchanged form is the guarantee.

This circumstance gives a peculiar interest to the study of minerals; it is one which impresses a feeling of awe and fascination akin to that aroused by an ancient manuscript or a work of art which survives as a permanent record of the artistic life and thought of bygone ages, and, further, it invests them with a unique value for the decipherment of the past.

There is one other aspect of mineralogy which I wish to emphasise. I have directed attention to the fatal sort of specialisation and exclusion to which the natural history school of thought tended; but let me repeat that mineralogy is, nevertheless, a branch of natural history, and that the proper study of minerals, as of all natural objects, is in itself a safeguard against specialisation.

The true mineralogist must bring to this pursuit the resources of all the sciences; one who is merely concerned with the physics or chemistry or crystallography of minerals makes only a one-sided study of the subject. The more intense and concentrated the work of the true mineralogist, the less confined will it be: in fact, the

more he specialises in mineralogy, the less of a specialist does he become.

For this reason, the natural history subjects have a very particular educational value; they deserve to hold their own for educational purposes, and not to be broken up into specialised sections. They have a particular value, not only as a stimulating introduction to chemistry or physics or biology as taught in schools to beginners, but also as a means of maintaining interest in those sciences at a later stage.

In young children, the instinct for collecting is strong, and equally strong is the desire to know something about what they collect; by many of them, the approach to science is most easily made through an interest in natural history.

At the later stage, many older boys and girls on the literary side in the upper forms of schools, whose main interest is outside science and who realise that it will not play a large part in their lives, boys and girls to whom prolonged teaching of chemistry, physics, and biology (especially if they are separated by watertight compartments) will be uninteresting, and therefore largely unprofitable might be made to retain their hold on the principles of all these fundamental sciences through the study of natural history.

We shall surely do well to utilise any interest that brings home to ordinary students the knowledge and conviction that science is not merely laboratory work, but that its principles are to be found in operation everywhere, though they may have to be explored in the laboratory. Those who specialise in language or history or literature must acquire this conviction by experience, just as those who specialise in science must learn by experience that all great literature is the expression of ideas, and that even scientific ideas cannot be expressed by an illiterate use of language.

A judicious employment of natural history will, I believe, do much to establish science in the place that it should occupy in our educational system.

When I accepted the invitation of the Council to deliver this lecture, I welcomed the opportunity it would give me of recalling to the Chemical Society this aspect of my favourite pursuit.

And, let me add, even for scientific workers in their later years a taste for natural history in any of its branches is worth maintaining as a very real corrective to narrow specialisation.

If an illustration be required, I cannot do better than remind you again of the wide scientific interests and achievements of the remarkable man whose name this lecture bears.

Mineralogy and botany appealed to his wide and catholic taste;

his love for minerals and plants was an abiding possession to him, not only because he loved them as beautiful things, but because he was a man deeply interested in natural objects and in the secrets of science that are revealed by them.

To those whose work lies in laboratories, such intercourse with nature is easily maintained, for there are many pathways that lead from experimental science to natural history.

Like Antaeus, they can always strengthen themselves by contact with Mother Earth, feeling with Wordsworth:

> "that Nature never did betray
> The heart that loved her; 'tis her privilege
> Though all the years of this our life to lead
> From joy to joy."

XXXII.—*The Synthesis of Ammonia at High Temperatures. Part II.*

By Edward Bradford Maxted.

In a recent paper (this vol., p. 168), the equilibrium between nitrogen, hydrogen, and ammonia at high temperatures was discussed from a thermodynamical point of view, and evidence was brought forward showing that in all probability the ammonia content of such a gas mixture in equilibrium, after decreasing with increasing temperature, eventually passes through a minimum and finally rises once more. On the basis of this theoretical indication of the possibility of a thermal synthesis of ammonia, it was shown experimentally that considerable yields of ammonia may be obtained by cooling a mixture of nitrogen and hydrogen extremely rapidly from the temperature of the oxy-hydrogen flame to that of the room.

In continuation of the above work, and especially in view of the known fact that a mixture of nitrogen and hydrogen may be completely converted into ammonia by sparking in a eudiometer over dilute acid (Donkin, *Proc. Roy. Soc.*, 1873, **21**, 281), an investigation was begun of the yields of ammonia obtainable from a rapidly cooled, high-tension arc, also by sparking, the present paper being a summary of the results obtained by induction discharge modified in such a way as to constitute a small, high-tension arc burning within a capillary tube, through which the mixture of nitrogen and hydrogen was passed.

By confining the action to a capillary tube, in the manner

described, the gas to be treated may be brought uniformly into contact with the discharge, and it was found easily possible to obtain at atmospheric pressure yields of ammonia amounting to 1·5 per cent. by volume of the gas-mixture taken for treatment. Induction sparks, as such, were found to exert a comparatively feeble action on the synthesis, energetic formation of ammonia only taking place when the electrodes were brought sufficiently close together to transform the ordinary spark discharge into a small, high-tension arc, accompanied by a visible and apparently continuous flame of high temperature.

Experimental.

The apparatus employed for the series of experiments about to be described consisted of a capillary glass tube having an internal diameter of 0·65 mm., an external diameter of 5 mm., and a length of about 10 cm. Platinum wire electrodes, 0·25 mm. thick, were sealed into the capillary tube in such a way as to leave a spark-gap of the size required, whilst the passage of gas through the tube was effected by means of fused-on glass side-tubes.

It was found inadvisable, on account of frequent fractures, to employ a heavy discharge, the most satisfactory conditions for the investigation being obtained with a "two-inch" coil, supplied with a primary current of from 3 to 3·5 amperes from the laboratory 220-volt main. Pure hydrogen and nitrogen for the synthesis were mixed in the proportion of three to one in a large gasholder and compressed into a cylinder for convenience in use. This mixed gas was passed at carefully determined rates through the capillary spark-gap, the ammonia formed being absorbed in dilute acid and estimated by means of Nessler's solution.

The first point to be investigated was the influence of the size of the spark-gap on the yield of ammonia, this gap being varied from 10 to 0·5 mm. while the rate of passage of the gas was first kept constant at 40 c.c. per hour, and, secondly, varied in such a way that the time of contact was kept at 0·0015 second for spark-gaps of various sizes. Table I summarises the results obtained by the first of these two methods, namely, with a constant rate of flow, table II those obtained by the second, that is, with a constant time of contact with the spark-gap, the primary current being in every case 3·5 amperes at 220 volts.

TABLE I.

Rate of Flow of Hydrogen–Nitrogen Mixture 40 c.c. *per hour.*

Length of spark-gap in mm.	Nature of discharge.	Percentage of ammonia by volume in issuing gases.
10	Spark	0·1
5	Incipient flame	0·25
1·5	Arc flame	0·8
0·5	Arc flame	1·1

TABLE II.

Estimated Time of Contact, 0·0015 *sec.*

Length of spark-gap in mm.	Nature of discharge.	Percentage of ammonia by volume in issuing gases.
10	Spark	less than 0·01
5	Incipient flame	0·04
1·5	Arc flame	0·5
0·5	Arc flame	1·1

It will be seen that as the size of the spark-gap is decreased, the flame loses its well-defined spark-like character and becomes a small but intensely hot high-tension arc, this flame, probably by virtue of its high temperature combined with the rapid cooling effect afforded by the relatively cold walls of the glass capillary tube, possessing the power of inducing the combination of nitrogen and hydrogen to an extent obtainable otherwise only by the action of a catalyst under a high pressure.   The rate of flow of the nitrogen–hydrogen mixture through the capillary tube was measured by allowing the gas issuing from the reaction tube to pass through a small, specially constructed gas-washing bottle, in which the ammonia was absorbed by very dilute sulphuric acid, the number of bubbles which formed per minute being counted and the volume of a bubble being known.   The estimation of ammonia in the resulting solution was carried out by means of Nessler's reagent.

It is difficult to estimate the temperature of the small high-tension arc formed, which, however, for the purpose of obtaining rough comparative figures for the various times of contact, has been assumed to be at approximately 3000°, but the effect of increasing temperature on the yield of ammonia formed is clearly seen.   This rise in yield with increasing temperature at high temperatures (in contradistinction from the decrease obtained at moderate temperatures) agrees with the results already reported. When working with small spark-gaps, a considerable deposit of platinum, removed from the electrodes by volatilisation and other

means, was obtained on the sides of the capillary tube, and in some cases the tube became fractured by the intense local heat, although in general the tube itself remained moderately cool, and in any case showed no tendency to soften.

The above results having demonstrated the necessity for employing as small a spark-gap as possible, in order to obtain the maximum local heating effect and consequently the maximum yield of ammonia, the effect of varying the time of contact with a spark-gap of constant small length (0·5 mm. and 1·5 mm.) was investigated. With an exceedingly small arc of the nature described, sufficiently rapid cooling for the retention of the ammonia formed is readily obtained by the action of the tube itself, the difficulty being rather the uniform heating to arc temperature of the comparatively rapid current of gas.

Table III demonstrates this point, it being found that any increase in the time of contact of the gas with the small arc, within the limits studied, causes a corresponding rise in the ammonia-content of the issuing gas.

TABLE III.

	Spark-gap in mm.	Velocity of flow in c.c. per hour.	Estimated time of contact in seconds.	Percentage of ammonia by volume in issuing gases.
(a)	0·5	97·2	0·0006	0·7
	0·5	40·5	0·0015	1·1
	0·5	18·9	0·0032	1·4
	0·5	15·0	0·0041	1·5
(b)	1·5	670·0	0·00027	0·25
	1·5	130·0	0·0014	0·5
	1·5	64·8	0·0028	0·6
	1·5	34·8	0·0052	0·87

The above results appeared to offer considerable encouragement for the investigation of the formation of ammonia by rapidly cooled high-tension arcs of a larger size. The results of such work will be communicated in a later paper.

XXXIII.—Atomic and Molecular Numbers.

By HERBERT STANLEY ALLEN.

ATOMIC NUMBERS.

ATOMIC weight and its determination have occupied a prominent position in the work of chemists since Dalton first put forward the Atomic Theory. Recent investigations in connexion with radio-

active elements and lead derived from radioactive substances have proved that the atomic weight has not the unique value hitherto attributed to it, and that a chemical element, such as lead, may be a mixture of "isotopes" occupying the same place in the periodic classification, but inseparable by chemical methods. Increasing importance is now being attached to the atomic number of an element, that is, the number which denotes the position of the element in Mendeléev's periodic table. As is well known, there are a few instances in which the place of the element is not in agreement with the atomic weight determinations; in such cases, the atomic number is given the value appropriate to the place in the table assigned by the chemical or physical properties. The values of the atomic numbers now accepted are given in table I, which follows the periodic classification of the elements commonly adopted. A better representation of the facts is obtained by employing a spiral in three dimensions. In this case, hydrogen may be placed at the pole of the spiral.

According to the electrical theory of matter, the atom consists of a central nucleus or core, carrying a resultant positive charge, surrounded by rings of negative electrons. It was first suggested by van den Broek that the number of the place in the periodic table was the same as the number of electrons in the atom or the number of unit charges carried by the nucleus. The same suggestion was made shortly afterwards by Soddy in connexion with the radioactive changes in the last thirteen places in the periodic table. The hypothesis is confirmed by the measurements of Barkla on the intensity of the X-radiation scattered from various substances. These indicate 7 electrons per atom of N, 8 for O, 6 for C, 16 for S, 1 for H. Rutherford's work on the scattering of a-particles by atoms of matter led him to the conclusion that the concentrated nuclear charge was approximately equal to half the atomic weight multiplied by the charge of an electron. The atomic numbers are, in fact, roughly equal to half the atomic weight.

It was, however, through the work of Moseley on the frequency of vibration of the X-rays, which are characteristic of the elements, that the importance of the atomic numbers was firmly established. The square root of the frequency of a line in the X-ray spectrum was found to be proportional to a number which increased by unity in passing from one element to the next in the periodic table. Thus every element from aluminium to gold may be characterised by an integer, N, which determines its X-ray spectrum. These atomic numbers were tabulated for the elements in question on the assumption that N for aluminium is 13. Between uranium and hydrogen, only five places remain vacant. For the rare earths,

PERIODIC SYSTEM OF THE ELEMENTS.

O	I	II	III	IV	V	VI	VII	VIII
	H 1							
He 2	Li 3	Gl 4	B 5	C 6	N 7	O 8	F 9	
Ne 10	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	
A* 18	K* 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26 Co* 27 Ni* 28
	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	
Kr 36	Rb 37	Sr 38	Yt 39	Zr 40	Cb 41	Mo 42	—43	Ru 44 Rh 45 Pd 46
	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te* 52	I* 53	
Xe 54	Cs 55	Ba 56	The Rare Earths 57—					
					Ta 73	W 74	—75	Os 76 Ir 77 Pt 78
	Au 79	Hg 80	Tl 81	Pb 82	Bi 83			
Nt 86		Ra 88		Th 90		U 92		

* Elements not placed in the order of the atomic weights.

which have not been tabulated in table I, Moseley found the following values for N: La, 57; Ce, 58; Pr, 59; Nd, 60; Sa, 62; Eu, 63; Gd, 64; Ho, 66; Er, 68.

It may now be regarded as certain that most of the properties of the elements depend on the value of the atomic number rather than on that of the atomic weight. For example, the atomic frequency which determines the thermal behaviour of the element in the solid state has been shown by the author (*Proc. Roy. Soc.*, 1917, [*A*], **94**, 100; *Phil. Mag.*, 1917, [vi], **34**, 478, 488) to bear a simple relation to the atomic number. Certain electronic frequencies are related to the atomic number in a similar way.

It will be noticed that Moseley's work does not give an unique determination of the value of N, since it is based on the assumption that N is 13 for aluminium. Rydberg has suggested that two unknown elements should be included in the periodic table between hydrogen and lithium, so that the atomic number of lithium would be 5 instead of 3. For all the elements later in the table, Rydberg's ordinals would be greater than Moseley's numbers by 2 units. Evidence in favour of Moseley's numbers is accumulating. Thus Barkla's results on the scattering of X-rays by air show that the number of electrons is as near to 7 for an atom of nitrogen as it is possible to estimate the pressure, of the air under which the experiments were made. In the work of the present author on the relation between atomic frequency and atomic number, it was found that the atomic numbers of Moseley gave more satisfactory agreement than did the atomic ordinals of Rydberg. The same conclusion was arrived at by van den Broek (*Phil. Mag.*, 1914, [vi], **28**, 630).

The atomic numbers express in a compact form many facts that have been long familiar to students of chemistry. They afford a striking confirmation of the statement of Chancourtois, made in 1863: "The properties of the bodies (elements) are the properties of number." Newlands assigned to the elements numbers (from 1 to 56) to indicate the order in which the elements must be placed when arranged in the ascending order of their atomic weights. He put forward the "law of octaves," according to which the numbers for members of the same family will differ by 7, or some multiple of 7, provided that the elements are not consecutive. Newlands admitted that it might be necessary to alter the number (7) separating analogous elements to some higher figure should a large number of new elements be discovered (compare Garrett, "The Periodic Law," 1909, Ch. III.). An examination of the atomic numbers of table I shows that in many cases the difference between the numbers for members of the same family is either 8

or some multiple of 8. In other cases, however, the difference is found to be 18. Thus in the case of the inert gases of the zero group, the atomic numbers for He (2), Ne (10), A (18) show differences of 8, whilst A (18), Kr (36), and Xe (54) show differences of 18. The interval between Xe (54) and Nt (86) is $32 = 4 \times 8$. In the case of subsidiary families of the same group, a common difference of 10 is manifest, for example, K (19), Cu (29), or Rb (37), Ag (47). The reason for these variations from the more commonly observed difference of 8 is the presence of three elements (for example, Fe, Co, Ni) instead of a single element in Group VIII of the table. The two extra elements change the common difference from 8 to 10 or from 16 to 18. Thus the law of octaves must be replaced by a new rule, which may perhaps be termed the rule of eight—a rule, however, to which there are quite definite exceptions (1) in the consecutive elements of Group VIII, (2) in the elements displaced two units by Group VIII, (3) in the metals of the rare earths.

MOLECULAR NUMBERS.

The author has suggested the introduction of the term "molecular number" to signify the sum of the positive charges carried by the atomic nuclei contained in the molecule. Thus the molecular number bears the same relation to the atomic number as the molecular weight bears to the atomic weight. When a molecule contains a atoms of an element A, b atoms of B, and c atoms of C, its chemical formula may be written $A_aB_bC_c$, whilst its molecular number will be $N = aN_a + bN_b + cN_c$, where N_a, N_b, N_c are the atomic numbers of the component elements. For example, the molecular number of water (H_2O, hydrol) is 10, for the molecule contains two atoms of hydrogen (nuclear charge, 1) and one atom of oxygen (nuclear charge, 8). Thus the C.G.S. system of units is a decimal system in a deeper and more intimate sense than its originators supposed, for it is based on the assumption that the gram is the mass of 1 c.c. of water at the temperature at which its density is a maximum. This fact probably accounts for the remarkable numerical relations, involving powers of 10, which the author has shown to exist between certain fundamental physical constants (*Proc. Physical Soc. London*, 1915, **27**, 425).

The four compounds, CH_4, NH_3, H_2O, HF, formed by the combination of hydrogen with a "typical" element belonging to successive groups in the second series of the periodic table, all have the same molecular number, 10. The corresponding elements in the third series of the table form compounds with hydrogen of the

same type, SiH_4, PH_3, H_2S, HCl, all having the molecular number 18 $(=10+8)$.

It may be remarked here that the molecular number is usually, but not invariably, an even number. This arises from the fact that when the valency is odd, the atomic number is usually odd also; but in the case of an element, such as copper, which may be either univalent or bivalent, or in the case of some of the metals of Group VIII the molecular number may be odd.

We have seen that the atomic numbers of analogous elements usually differ by 8 or a multiple of 8, or in some cases by a number that is 2 units greater than one of the foregoing. It is obvious that results of a similar character are to be expected in dealing with the molecular numbers of analogous compounds. The halogen compounds of the alkali metals may be considered by way of illustration. The results are collected in table II, the figures in italics being the differences between the molecular numbers in adjoining rows or columns.

TABLE II.

Element.	F 9 Fluoride.		Cl 17 Chloride.		Br 35 Bromide.		I 53 Iodide.
Li 3	12	8	20	18	38	18	56
	8		8		8		8
Na 11	20	8	28	18	46	18	64
	8		8		8		8
K 19	28	8	36	18	54	18	72
	18		18		18		18
Rb 37	46	8	54	18	72	18	90
	18		18		18		18
Cs 55	64	8	72	18	90	18	108

The molecular number of a cuprous haloid exceeds by 10 that of the corresponding potassium compound, and similarly the molecular number of a silver haloid exceeds by 10 that of the corresponding rubidium compound.

In the case of an element which has a valency greater than 1, the results may be more complicated, since one or more of the atomic numbers may require multiplication by a numerical factor depending on the number of atoms in the molecule. For compounds containing only elements from $N=1$ to $N=25$, however, comparatively simple results will be obtained, since the divergences due to the three elements in Group VIII do not then appear.

Instead, of the law of octaves, we have what has been termed the rule of eight holding, with certain exceptions, in connexion with the molecular numbers of analogous compounds.

The value of N for a compound radicle can be calculated in the same way as for a complete molecule. Thus for the ammonium group (NH_4), the value of N, which may be called the group

number or the radicle number, is 11. It is noteworthy that this is the same as the atomic number of sodium, which can be replaced by the ammonium group in so many of its compounds. The principle here involved may be extended, and we may say that in a chemical compound one radicle may frequently be replaced by another having the same number, or a number differing from the first by 8 or a multiple of 8.

The hydrogen molecule, H—H ($N = 2$), may be regarded as the typical simple molecule, from which a large number of chemical compounds may be derived by substituting for one or both of the hydrogen atoms another atom or radicle.

Thus water may be looked on as a typical compound in which one atom of hydrogen ($N = 1$) is combined with the hydroxyl group, OH ($N = 9$). The hydroxyl group may be replaced by CH_3, NH_2, F, for each of which $N = 9$, giving rise to the compounds methane, ammonia, and hydrogen fluoride. Again, in each of these compounds the hydrogen atom may be replaced by one of the groups mentioned, giving rise to such compounds as C_2H_6, $CH_3 \cdot OH$, N_2H_4, $NH_2 \cdot OH$, H_2O_2, for which the molecular number is $9 + 9 = 18$.

Owing to the fact that the group number of $\cdot CH_2 \cdot$ is 8, the rule of eight is prominent in the case of organic compounds. In open-chain compounds, the addition of each CH_2-group means an increase of 8 in the molecular number.

It is necessary to enter a caution as regards the interpretation of the results when dealing with a chemical group or radicle. The "group number" may be taken to represent the sum of the charges of the atomic nuclei of the group. It will only represent the number of negative electrons associated with the radicle as well when the radicle, considered as a whole, is not charged or electrically neutral. According to the views of Sir J. J. Thomson (*Phil. Mag.*, 1914, [vi], **27**, 768), the radicle may be charged either positively or negatively, and in such a case the number of negative electrons will differ from the radicle number here given.

The molecular numbers here discussed, and the relations between them, are not mere arithmetical curiosities. It is to be remembered that the molecular number is associated with a perfectly definite physical conception, namely, the number of unit charges found in the positive nuclei of the atoms in the molecule or the number of the complementary negative electrons. It is to be anticipated that the molecular numbers will play an important part in determining the physical or chemical characteristics of molecules or radicles. Some progress, in fact, has already been made in establishing such a connexion. It has been shown by Nernst and others that the thermal behaviour of a compound in

the solid state depends on a certain characteristic frequency or frequencies. The author has found (*Phil. Mag.*, 1918, [vi], 35, 338) that simple relations exist between the products obtained by multiplying such a frequency and the molecular number of the compound. Thus there must be an intimate connexion between the specific heat and the molecular number.   In the author's opinion, it is safe to predict that other physical properties of chemical compounds will be found to depend on the values of the molecular numbers.

<div style="text-align:center">

KING'S COLLEGE,
UNIVERSITY OF LONDON.   [*Received, January 18th*, 1918.]

</div>

XXXIV.—*Reactions between Solid Substances.*

By LESLIE HENRY PARKER.

IN a previous communication by the author (T., 1914, **105**, 1504), it has been shown that under certain conditions it is possible to bring about interaction between various pairs of solid substances by means of shearing stress, even at ordinary temperatures, or at least very greatly to increase the velocity of these reactions above that which normally pertains at these temperatures.   The experiments described in that paper led the author to the conclusion that shearing stress, such as could be applied by hand between a pestle and mortar, is widely different in its effects from simple pressure, and that one of the main reasons why it is able to bring about reactions between apparently solid substances is that local or surface fusion of the reacting substances is occasioned.

This phenomenon seemed of sufficient interest to warrant further study, as it is a well-known fact that salts in the fused state are capable of reacting together.

In considering the conditions under which solid salt pairs are capable of reacting, it has to be remembered that most of the ordinary salts melt at a temperature that is high compared with that at which one commonly works with these substances; moreover, that a slight rise in temperature very often occasions a very rapid increase in the reaction velocity between two substances. From this it follows that the readiness with which two salts react in the fused state may be due to the influence of one or both of the following factors, namely, (1) the *high temperature* necessary

to bring one or both of the salts into a state of fusion, or (2) the existence of one or both of the salts in the *liquid state*, and the intimate contact occasioned thereby.

The object of the present investigation was to attempt to gain some idea of the relative importance of these two factors, because if high temperature is the main influence in causing two salts to react, some further agency must be looked for than mere fusion when reactions are brought about under shearing stress. If, on the other hand, the existence of the liquid state is the predominating influence, there appears to be no reason why salts should not react with appreciable velocity at ordinary temperatures should one or more of them be brought into a state of fusion, however transitory.

An investigation was therefore commenced ·on the velocity of reaction between various salt pairs at temperatures up to and through the melting point of the mixtures. The form of the curve obtained by plotting velocity of reaction against temperature should give information on the point desired.

Let us suppose that the temperature is the main influence in accelerating the velocity of reaction. The latter will go on increasing as the temperature rises until the melting point of the mixture is reached. At this point, however, there should be no marked increase in velocity, as we have assumed the existence of the liquid state to be of secondary importance. The curve should therefore exhibit no discontinuity at this temperature, but pass smoothly through the melting point.

On the other hand, let us suppose that the existence of the liquid state is of greater importance to the progress of the reaction. There may be, and probably will be, an increase of reaction velocity between the two mixed salts while still both in the solid state. When the point of fusion of the mixture is reached, however, there will be a sudden increase in the reaction velocity, and the curve will exhibit a sudden break at this temperature.

EXPERIMENTAL.

Sodium Carbonate and Barium Sulphate.

The interaction between these substances has already been investigated under shearing stress, as described in the previous paper (*loc. cit.*).

10·6 Grams of sodium carbonate, prepared from purified sodium hydrogen carbonate and dried by prolonged heating, were mixed with 23·34 grams (equivalent quantity) of barium sulphate, precipitated from purified barium chloride, and dried by heating in a current of dry air. The two salts were placed in a dry, air-tight

bottle, stirred with a glass rod, and shaken for fifteen minutes to mix them thoroughly. An arbitrary sample of this mixture was then taken for analysis.

A quantity equivalent to 1·06 grams of sodium carbonate (3·394 grams) was weighed out, treated with cold water, and lixiviated through a specially prepared Gooch crucible, the filtrate being treated with N- and $N/10$-hydrochloric acid, as previously described (*loc. cit.*). An amount of acid was neutralised corresponding with exactly 1·06 grams of sodium carbonate, showing that the original mixture was homogeneous and not affected by water. If sufficient care were taken to ensure that the salts were in a fine state of subdivision, and that they were stirred (not ground) and shaken together sufficiently, this method of sampling gave a similar result with many other experiments. No variation in the composition of the mixture in various parts was therefore to be feared, especially as only sufficient mixture was made up at any one time for nine experiments and one sample.

A nickel boat was then constructed to accommodate, when about half full, 3·394 grams of the mixture. This was heated to various temperatures for various lengths of time in an electric furnace, constructed by winding about 900 cm. of nichrome wire (4·1 ohms per metre) on 20 cm. of opaque silica tubing of 4·4 cm. internal bore. This was insulated with about six turns of asbestos paper and two turns of asbestos cloth. The ends were closed with asbestos card, and the whole was connected with a 110-volt lighting circuit, when suitable temperatures, as registered by a thermo-element, could be obtained and adjusted by variable resistances.

The procedure for each experiment was to heat the furnace to the required temperature, open one end, quickly insert the boat

TABLE I.

Time in minutes.	Sodium carbonate transformed. Per cent.							
	105°	210—215°	310°	360°	400°	500°	600°	680—685°
30	0·55	0·48	1·07	0·96	1·37	8·42	30·5	48·1
60	1·37	0·30	1·31	1·25	2·27	11·7	34·4	52·8
90	—	1·19	1·97	2·26	3·34	11·1	37·6	57·6
120	—	1·37	2·62	—	3·64	13·1	40·6	58·8
150	0·55	—	2·98	—	3·94	13·2	44·0	—
180	—	1·79	—	—	—	—	—	—
210	1·37	1·79	—	2·86	3·76	17·4	46·3	60·6

	700—720° (fusion).
2	60·0
5	60·6
10	60·0
30	59·2

containing the mixture, so adjusting its position in the middle of
the furnace on some silica supports that it was clear of the walls
of the furnace and almost touching the thermo-element, and close
the furnace for the required time. At the expiration of a definite

FIG. 1.

period, the boat was withdrawn and the residual sodium carbonate
was estimated. The results are shown in the table on p. 398.

These results are expressed graphically in Fig. 1.

It will be noticed that this mixture fuses at about 720° (as

registered by the thermo-element used), and in this state the velocity of reaction, so far as can be seen, is practically instantaneous, equilibrium being set up for the reaction

$$Na_2CO_3 + BaSO_4 \rightleftharpoons BaCO_3 + Na_2SO_4$$
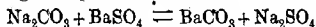
when about 60 per cent. of the sodium carbonate is transformed.

It will also be remarked that up to 400°, the amount of sodium carbonate that has entered into reaction with the barium sulphate is insignificant, even after three and a-half hours. What little double decomposition has occurred has taken place fairly regularly, and it is fairly easy to compute the average reaction velocity for the temperatures up to 400°. The curves for 500°, 600°, and 685°, however, show some peculiarities. It will be noticed that during the first thirty minutes, in each case the reaction has started fairly rapidly, but after this time, has slowed down to a regular velocity, the points lying practically on a straight line.

This might be explained by the presence of a trace of moisture occluded in the particles of the salts, which is always very difficult to remove. At the high temperature of the experiments, this is rapidly expelled, but causes a certain amount of reaction between the salts on its own account. Once driven off, however, its influence is lost, and the straight part of the curve represents the true velocity of reaction between sodium carbonate and barium sulphate at any particular temperature.

It is possible that this moisture may have occasioned the small amount of change at the lower temperatures, and that had it been possible completely to dry the salts, the velocity of reaction up to 400° would have been negligible. In the curve for 685°, the portion between the points A and B has been taken as representing the reaction velocity, as the point C represents equilibrium, which was probably attained before the time represented in the figure (210 minutes). If we now plot reaction velocity against temperature, we obtain the curve shown in Fig. 2 (continuous line), which is remarkably regular up to the point for 720°, when, the velocity of the reaction at that point becoming instantaneous, a sudden break in the continuity of the curve occurs.

If the equilibrium of this system is considered, it will be seen that in the solid state there are present four solid phases, which can be defined by three components. This gives one degree of freedom for the system, and the equilibrium is therefore determined by the temperature; it is therefore probable that there is a definite equilibrium mixture for each temperature, and that the lower curves in Fig. 1 would not all of necessity approach the equilibrium attained on fusion, namely, the transformation of 60 per cent. of the sodium carbonate.

It was also endeavoured to reconcile the velocity–temperature curve in Fig. 2 with the formula put forward by Arrhenius and van't Hoff, namely,

$$\frac{d \log k}{dT} = \frac{A}{T^2} + \frac{B}{T} + C.$$

The dotted curve in Fig. 2 is that given by the formula

$$\log k = \frac{1988}{T} + 11{\cdot}24 \log T - 36{\cdot}332.$$

Fig. 2.
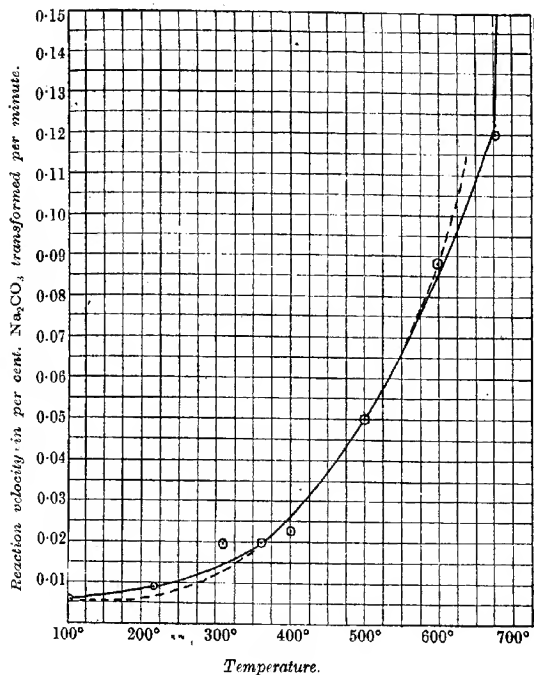
which follows the experimental curve very closely except at the higher temperatures as the point of fusion is approached.

The next two cases were chosen to be of such a nature that no limiting equilibrium could be obtained, it being possible for the reaction to proceed to completion in one sense.

Silver Nitrate and Sodium Carbonate.

The products of this interaction are silver carbonate and sodium nitrate, and as the former is unstable, decomposing with rapid evolution of carbon dioxide at 100°, the rate of evolution of this gas from a mixture of silver nitrate and sodium carbonate could be used as a measure of the velocity of reaction between these two salts. The reaction may be regarded as capable of proceeding to completion in the sense

$$Na_2CO_3 + 2AgNO_3 = 2NaNO_3 + Ag_2CO_3,$$
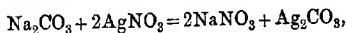
as the only equilibrium which can be established is that between silver oxide and carbon dioxide, which may be neglected.

Silver nitrate crystals were purified by recrystallisation from dilute nitric acid solution and dried by heating just above the fusion point for two hours. The sodium carbonate was prepared and purified as before. The apparatus employed in these experiments consisted of a thick Jena-glass test-tube, somewhat longer than the electric furnace used to heat it, with a tube of soft glass ground into its open end. This tube was sealed to the gauge column of a Sprengel exhaust pump. The mixture of silver nitrate and sodium carbonate (always 1·699 grams of the former and 0·53 gram of the latter) was placed in a porcelain boat, which was then introduced into the Jena-glass tube. This was then connected to the pump, the apparatus exhausted, and the Jena-glass tube and contents were heated by the electric furnace. The rate of fall of the manometer on the pump was noted, giving a measure of the velocity of reaction proceeding between the mixed salts. The salts were tested for occluded gases by being heated separately in a vacuum. No appreciable fall in the mercury was to be noted. In any series of readings taken at any particular temperature, after the last reading the tube and contents were allowed to cool to the ordinary temperature, when the manometer was again read, and all previous readings for that experiment were corrected accordingly, thus eliminating the effect of the various temperatures on the partial pressure of the carbon dioxide. The results are shown in the table on p. 403.

These results are expressed graphically in Fig. 3.

The characteristics previously noted are again in evidence. After a short period of induction over the first five minutes, due no doubt to the gradual heating up of the mixture, the curves for the temperatures between 110° and 170° show an increasing rapidity for the reaction at the start, over a period of about a

TABLE II.

Time in minutes.	Corrected partial pressure of carbon dioxide in mm. of mercury.					
	90°	110°	130°	155—160°	165°	170°
10	—	—	0·5	1·8	2·7	15·3
15	—	—	—	—	12·6	30·6
20	—	—	4·5	12·9	22·4	42·3
25	—	—	—	—	28·6	50·4
30	1·0	5·5	9·5	20·2	34·0	53·7
60	1·8	12·7	17·2	32·2	43·8	63·0
90	3·7	15·8	20·0	37·7	48·3	69·3
120	—	17·0	—	41·4	52·8	—
150	5·5	18·0	29·0	45·0	57·4	77·4
180	—	19·0	29·0	46·0	60·0	81·0
210	8·2	—	—	—	—	—
270	9·6	—	—	—	—	—
300	10·5	—	—	—	—	—

Time in minutes.	Corrected partial pressure of carbon dioxide in mm. of mercury.	
	180° (fusion).	240—250° (fusion).
5	3·2	1·8
6	7·2	3·7
7	13·6	6·4
8	25·4	10·1
9	59·7	14·7
10	97·0	26·6
10½	112·0	43·1
11	125·0	62·4
11½	135·0	89·0
12	146·0	114·0
12½	157·0	134·0
13	168·0	153·0
13½	180·0	170·0
14	191·0	186·0
14½	202·0	205·0
15	211·0]	221·0
15½	219·0	237·0
16	225·0	
16½	230·0	
17	235·0	
17½	239·0	
18	243·0	
19	247·0	

further fifty minutes. After that time, the rate of reaction in each case becomes practically uniform.

The curves for 180°, where fusion took place, and for 245°, although apparently almost coincident on the diagram at the scale given, are by no means so in reality. Calculated from the figures in table II, the curve for 245° represents almost twice the reaction velocity as does the curve for 180°.

The graphical representation of reaction velocity against tempera-

R*

ture is shown in Fig. 4, and again a sudden increase is to be noted at the temperature of fusion.

In the solid state, there are here present five phases, comprised of four solid phases ($AgNO_3$, Ag_2O, $NaNO_3$, Na_2CO_3) and one gaseous phase (CO_2); all these are defined by the four components Ag_2O, Na_2O, N_2O_5, and CO_2. The pressure of the system is there-

Fig. 3.

$AgNO_3 + Na_2CO_3$

Time in minutes.
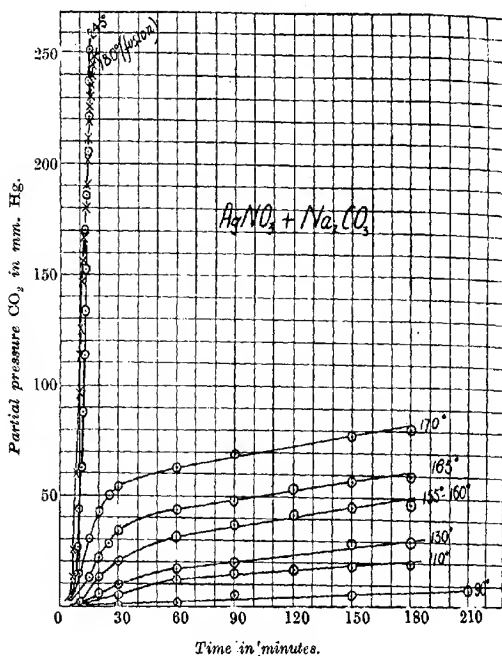
fore a function of the temperature, an example of the active masses of the reacting substances remaining constant in the solid state.

In the partly fused state there exist four solid phases, one liquid phase, and one gaseous phase, with the same number of components as before. There are, therefore, no degrees of freedom, and the point K is analogous to the triple point in the system ice-water-water vapour.

Cuprous Chloride and Sodium Carbonate.

This mixture was chosen more from the point of view of dis-
covering what happened after fusion than actually at the fusion
point. The cuprous chloride was prepared from the commercial
substance by dissolving it in concentrated hydrochloric acid and
pouring the solution into water. The precipitated salt was quickly

Fig. 4.
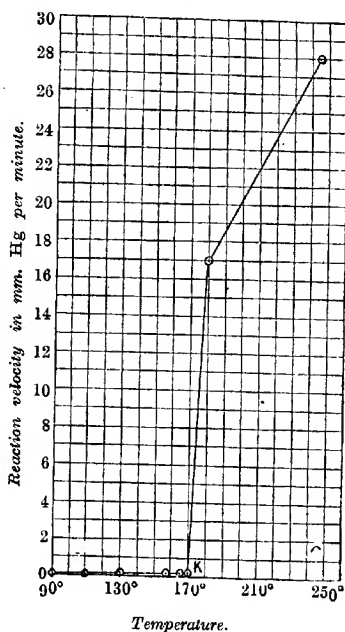
collected, washed with alcohol and ether, and dried for many hours
at 100°.

It remained quite white, apparently indefinitely, in a dry, air-
tight bottle. For each determination, a mixture of 0·991 gram of
this salt with 0·53 gram of sodium carbonate was taken (equivalent
quantities), and the experiments were conducted with the same
apparatus as in the last reaction. The results are shown in the
following table.

R* 2

TABLE III.

Time in minutes.	Corrected partial pressure of carbon dioxide in mm. of mercury.			
	100°	150°	200°	260°
5		3·3	1·8	3·6
10		7·5	8·2	48·0
11		—	—	83·0
12		—	—	116·0
13		—	—	147·0
14		—	—	174·0
15		10·0	20·0	199·0
16		—	—	217·0
17		—	—	234·0
18		—	—	249·0
19		—	—	259·0
20		13·3	38·0	268·0
25		—	59·0	310·0
30		15·8	77·0	336·0
40		17·5	97·5	376·0
50		20·0	113·0	—
60		20·8	127·0	419·0
90		25·0	164·0	—
120		—	195·0	—
150		—	208·0	—
180	nil	—	230·0	—

	300°	330°	350°
5	7·3	17·5	9·2
6	18·4	24·0	35·0
6½	—	35·0	68·0
7	53·0	53·0	119·0
7½	83·5	84·0	178·0
8	119·0	123·0	256·0
8¼	138·0	141·0	307·0
8½	155·0	163·0	353·0
8¾	172·0	181·0	404·0
9	192·0	200·0	454·0
9¼	207·0	217·0	—
9½	223·0	238·0	521·0
9¾	237·0	258·0	—
10	250·0	281·0	569·0
10¼	262·0	306·0	—
10½	274·0	334·0	—
10¾	283·0	361·0	—
11	291·0	389·0	—
11¼	—	420·0	—
11½	309·0	446·0	—
11¾	—	471·0	—
12	324·0	497·0	—
12¼	—	515·0	—
12½	338·0	531·0	—
12¾	—	548·0	—
13	350·0	—	—
13½	362·0	—	—
14	370·0	—	—

These results are expressed graphically in Figs. 5 and 6.

Fusion took place at about 260°, causing a large increase in the reaction velocity.

It seems fairly well established, therefore, that the process of fusion of itself causes a marked increase in the reaction velocity of the mixtures, the ratio of velocity in the liquid state to that at the highest temperature in the solid state varying from infinity

FIG. 5.

Time in minutes.
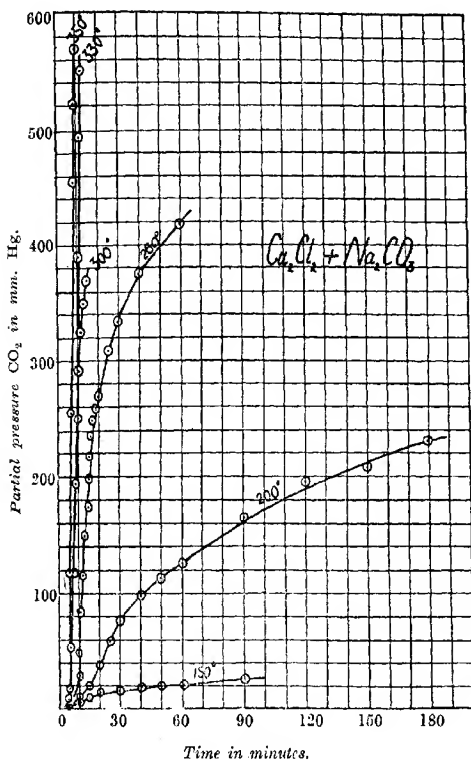
in Case 1, through about 150 in Case 2, to about 20 times in Case 3.

It may be taken, therefore, that the liquid state *per se* has a direct bearing on the interaction of salt pairs. It should be noted, however, that after fusion the velocity of reaction is not quite so

independent of the temperature as in the solid state. The velocity becoming practically infinite on fusion in Case 1, this could be investigated no further, but in Cases 2 and 3 it is seen that further rise in temperature causes a further great increase in reaction velocity, although not nearly so great as the increase pro-

FIG. 6.
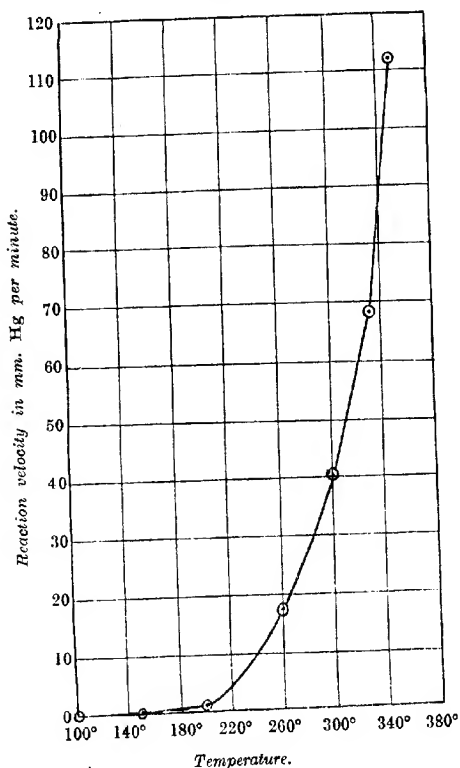
Temperature.

duced by fusion over the velocity in the solid state. In Case 2, a rise of 65° nearly doubles the reaction velocity, and in Case 3, a rise of 90° multiplies the rate about six times. The reacting molecules now being in intimate contact, the temperature begins to exert a well-defined influence.

There seems therefore to be no inherent objection to the explanation, put forward in the previous communication, of the reactions brought about by shearing stress between apparently solid substances, namely, that the stress causes local or surface fusion of the salts; it has been shown that the liquid state, quite apart from temperature effects, has an important bearing on the capacity for interaction.

It is known that the size of particle may have a slight influence on the melting point of a substance, as in the case of salol investigated by Pavlov (*J. Russ. Phys. Chem. Soc.*, 1910, **40**, 1022), who showed that the temperature of fusion was, however, only lowered 2·8° for one hundred times the increase of surface (ten times decrease of radius). This therefore is probably a factor of no great magnitude.

Tammann (*Ann. Phys. Chem.*, 1899, [ii], **68**, 553, 629) showed that simple pressure was capable of influencing the melting and transition points of a large number of substances. He also showed *Zeitsch. physikal. Chem.*, 1903, **46**, 818) that the fusion curve for sodium sulphate rose to a maximum at a pressure of 750 kilos. per sq. cm., and then fell considerably.

Most inorganic salts, however, have their fusion points raised by increase of pressure, and even in cases of the reverse, such as that of silver bromide, it is necessary to apply pressures of the order of 10^5 atmospheres to cause fusion at ordinary temperatures. Although the experimental facts do not yet seem to offer a complete explanation of the action of shearing stress as applied to solid substances, it thus appears probable that such stress has a peculiar action of its own towards the production on the surface of such materials of a state analogous to, if not identical with, fusion.

XXXV.—*The Association of Organic Compounds in Benzene and Alcohol Solution as Determined by the Vapour Pressure Method.*

By WILLIAM ROSS INNES.

IN a previous paper (T., 1902, **81**, 682), the author has described the results obtained in an investigation on the influence of temperature on association in benzene solution by Raoult's ebullioscopic method.

The investigation was undertaken chiefly with the view of discovering the cause of the very different behaviour of the acids and oximes on the one hand, and the anilides, alcohols, and phenols on the other, in hydrocarbon and other solvents, generally spoken of as associating solvents.

It seemed probable that if the different behaviour of these two classes of compound could be explained, some light would be thrown on the nature of association.

As is well known, the acids and oximes give data in dilute solution which indicate that the molecular weight is normal at extreme dilution; with increasing concentration, the value for the molecular weight rises, at first rapidly, then more slowly, until it reaches double the normal value; further increase of concentration affects the value but little in most cases.

Anilides, alcohols, and phenols behave quite differently, the molecular weight increasing, generally, almost linearly, and there is no indication of the molecular weight reaching a limit, even at the highest concentrations at which it is usual to carry out determinations by the cryoscopic and ebullioscopic methods.

The investigation failed in its main objective, and it was evident that more concentrated solutions would have to be examined in order to arrive at the desired result.

The reverse problem, namely, the behaviour of substances belonging to "the associating group of solvents" in alcohol, also seemed worthy of investigation.

It was decided to use the vapour-pressure method in this investigation. If the experimental results obtained by Raoult in ethereal solution by the vapour-pressure method are plotted to show molecular weight against concentration, the regularity of the curves, apart from the determinations in dilute solution, suggests that the statical method used is much more accurate than references to it in literature would lead one to suppose, and that little is needed to make it a satisfactory one.

It was originally intended to use the statical method. With Ramsay and Young's apparatus (*Phil. Trans.*, 1887, **178**, 57), the temperature could be varied over a wide range, and it was hoped, by boiling out the tube and stirring the solution, so as to prevent varying concentration at the free surface by evaporation or condensation of the solvent, that accurate results would be obtained. While the pressure apparatus was being made, the experiments described in the following pages were commenced, and the method gave such satisfactory results that it was continued until other work prevented the completion of the investigation.

The apparatus employed was essentially the same as that used in the ebullioscopic method (T., 1902, **81**, 685), except that the jacket of the boiling tube was not connected to the constant pressure apparatus, but to a separate reservoir with manometer and pump, so that the temperature of the jacket could be kept approximately at the temperature employed. A temperature about $3°$ higher than that of the boiling tube was aimed at. For the experiments at $75°$, alcohol boiling under atmospheric pressure was used. The tube L of the regulator was graduated, so that the apparatus could be set to give the pressure required, and was fitted with a micrometer screw allowing of ready adjustment to $0·1$ mm. or less. A barometer, trapped to prevent entrance of air to the upper part, stood in the same trough as the manometer H, and the difference in height was read on a millimetre mirror scale. This difference is, of course, the pressure in the apparatus, and is independent of the atmospheric pressure. A set of thermometers reading to $0·1°$ with open scale, made by Hicks, was used. They were not calibrated, as they were employed merely as zero instruments. That they were accurate and that the zero altered very little is shown by the vapour pressures obtained for benzene and alcohol at different temperatures. The exact temperatures are, of course, given by the vapour pressure of the solvent. In order to prevent changes of pressure affecting the volume of the thermometer bulb, the thermometer was placed in a tube fitting it closely and containing enough mercury to cover the bulb.

The boiling tube was of such size that from about 15 to 50 grams of solution could be used. It was of lead glass, and no platinum was fused through the bottom. It was packed with beads and platinum clippings, as already described (T., 1901, **79**, 262). The end of the condenser of the boiling tube was connected to a tube dipping into a fractionating flask to act as a trap in case of sudden frothing, and the side-tube of the fractionating flask passed into a drying tube which joined on to the constant-pressure apparatus. In order to obtain satisfactory results, it was found necessary to

take every possible precaution to exclude traces of moisture from the apparatus and chemicals.

The benzene used contained a trace of thiophen, it was of perfectly constant boiling point, and was dried over phosphoric oxide. The alcohol was finally dried with phosphoric oxide and distilled. It was of constant boiling point. The benzene and alcohol were kept in bottles, through the corks of which pipettes passed, the upper end of the pipette passing into a drying tube. The solvent was measured out in all cases.

Most of the substances were bought in a sufficient state of purity for use; a few were further purified. The dimethyl tartrate and β-benzilmonoxime were prepared.   The substances were in most cases melted and cast in a glass tube. When solid, the tube was heated and the rod of substance pressed out. β-Benzilmonoxime could not be satisfactorily treated in this way and did not form pastilles readily; it was partly melted, allowed to cool, and broken into pieces of suitable size. The substances were prepared for use a day in advance and kept in a vacuum over sulphuric acid until required.

Method.

The boiling tube containing the solvent is connected to the constant-pressure apparatus, the regulator set to give approximately the pressure required, and the apparatus exhausted. When the pressure has fallen and the regulator begins to act, the gas is lit and adjusted to such a height that the benzene boils briskly. It is essential that boiling should be fairly rapid, otherwise in concentrated solutions layers of different concentration form and cause very large errors. After the solvent has been boiling for a few minutes, the regulator is altered until the temperature is that required (t°), and the apparatus left for an hour; if necessary, a further adjustment is then made, the barometer and manometer are read, and boiling is continued for a further ten minutes. If temperature and pressure are both constant, the first addition of solute is introduced in the manner already described (*loc. cit.*), the regulator being altered so as to lower the pressure by the amount which it is expected the vapour pressure will be lowered. When solution is complete, the pressure is altered until the temperature (t°) is again obtained, and the solution allowed to boil for ten minutes; a further adjustment is made if necessary, and the solution allowed to boil for a further ten minutes until constancy is obtained; the pressure is then read.   Additions are then made under similar conditions until the concentration is about 50 per cent.

Beyond 50 per cent., very large additions have to be made to increase the concentration in the steps required. A fresh series was then started with 10 c.c. of solvent. The pressure of the solvent was determined as before, sufficient solute added to give a concentration of 50—60 per cent., and the additions continued as before up to 80 per cent.

In some cases, where only one series was carried out at a given temperature, 15 c.c. of benzene were used, and, after determining the vapour pressure, sufficient solute was added to cover completely the thermometer bulb. A range of concentration from about 15 to 70—80 per cent. was thus attained in one series. Beyond 80 per cent., determinations were made by weighing into the boiling tube a suitable amount of solute, a small amount of benzene was added, and the vapour pressure determined after the temperature had become constant; further additions of benzene were then made. In order to do this, the clip p was closed, the flame under the boiling tube removed, and the addition of benzene made with a long pipette. Before reopening the clip p, the pressure in the apparatus is increased considerably by opening the cock e, otherwise frothing would occur, and the clip is opened gradually to avoid loss of benzene vapour as much as possible. The regulator is moved to give a higher pressure, and the flame put back. At 75°, the pressure was allowed to become equal to the atmospheric. In this way, it was possible to work from a concentration of 95 per cent. downwards. At the highest concentration, a constant temperature was not attained. With azobenzene there was a very slow variation of a few tenths of a degree about a mean position. The determination took a very long time, owing to the extreme slowness of the temperature change. The method is not a practical one at a concentration of 95 per cent.; at 90 per cent., however, the difficulty almost entirely disappears with azobenzene as solute. Only two substances were examined at these concentrations, namely, the "normal" azobenzene and the very abnormal dimethyl tartrate. The determinations with dimethyl tartrate at these great concentrations were much more difficult than with azobenzene, especially in the determinations above 60 per cent. molecular concentration at 75°. The only method by which determinations could be made was to follow the change of temperature with corresponding change of pressure until the temperature remained constant for a time. In this way, a higher and lower limit of the vapour pressure was obtained. Owing to the slowness with which the temperature altered and the variation in the limit, it was not practicable to take a mean. The largest pressure, that is, the pressure corresponding with the highest molecular weight, was

taken in each case. Although the possible error in these deter-
minations is large and not much value can be attached to the
individual values, it seems fair to assume that the real molecular
weights are not greater than those calculated.

At 53°, the temperature variation was much less than at 75°,
and single determinations were carried out instead of series, so
that the variations could be observed over sufficient time to take
a mean. Even under these conditions, the experimental error
appears to be large, the two determinations at nearly the same
concentration showing a large difference in molecular weight.

In the determination at 63°, the temperature remained almost
constant throughout the time ordinarily devoted to a series.

There seems little doubt that the variation of temperature in
these experiments is due to the difficulty with which the benzene,
returned from the condenser, mixed with the highly viscous solu-
tion, whilst the greater constancy at the lower temperatures may
be due partly to the more efficient stirring of the larger bubbles
of vapour formed at the lower pressure and partly to the smaller
amount of benzene vapour condensed for similar rates of boiling.

Results.

The results obtained are given in tabular form on p. 430 *et seq.*

Col. I. gives the temperature at which the series was carried
out, as indicated by the thermometer $= t$.

II., the observed pressure of the solvent, no corrections being
made $= p$.

III. $p - p'$, also without any correction.

IV., weight of solvent actually taken $= G$.

V., weight of solute $= g$.

VI., grams of substance per 100 grams of solution

VII., the percentage molecular concentration, $100n/n + N$.

VIII., the molecular weight found $= m'$.

IX., the association factor m'/m.

In calculating VI., VII., VIII., 0·4 gram is subtracted from the
weight of the solvent in the experiments at the higher pressures
and 0·3 gram in those at the lower pressures, to allow for the
amount of solvent in the state of vapour and that wetting the
walls of the tube above the solution.

The vapour-pressure method offers the advantage that a series
of determinations at different concentrations can be carried out
isothermally, whilst the great simplicity of the vapour pressure
law for concentrated solutions of "normal" substances suggests
that it will be easier to interpret the experimental results obtained

with more complex systems, where present-day theory offers little guide, than would be the case by the cryoscopic, ebullioscopic, or osmotic methods.

The vapour pressure law was first established experimentally by Raoult for non-volatile solutes in a volatile solvent, and was shown by him to apply satisfactorily for a number of solutes in ethereal solution even up to 80—90 per cent. concentration. It is, however, from the study of mixtures in which both constituents are volatile that the accuracy of the law has been experimentally established. It has been shown that for mixtures of non-associated, closely related liquids, the so-called ideal solutions, the law holds with great accuracy and within the limit of experimental error throughout the whole range of concentration from 0—100 per cent.

Raoult's law $\dfrac{p-p'}{p} = \dfrac{n}{N+n}$ is readily transformed algebraically into (2) $\dfrac{p-p'}{p'} = \dfrac{n}{n}$ and (3) $p' = p\dfrac{N}{N+n}$, on the assumption that n has the same value in both numerator and denominator, the last form being that most convenient for considering solutions in which both constituents are volatile, whilst (2) is a convenient form for calculating the results obtained with non-volatile solutes.

Where both constituents are volatile, it is evident that the distinction between solute and solvent entirely disappears, since for each constituent its partial pressure is proportional to the product of its pressure in the pure state and its molar fraction in the solution. The same must be true where the vapour pressure of one of the constituents of the solution is negligibly small, since this is merely a limiting case of the more general relation. It is therefore purely arbitrary which constituent we call solvent and which solute. In this communication, that constituent which separates in the pure state—as vapour in the vapour-pressure and ebullioscopic methods, as ice in the cryoscopic method—is referred to as the solvent, whatever its concentration in the solution.

The vapour pressure law has been deduced thermodynamically by several methods for two classes of solutions, namely, ideal solutions of any concentration and infinitely dilute solutions.

In deducing the law for ideal solutions, one of the simplifying assumptions that has to be made is that the constituents of the solution are not associated as pure liquids, and that no association takes place on mixing them. It is evident that the law thus derived becomes purely empirical when applied to associated solutions. That such an assumption has to be made does not show that the vapour pressure law is not applicable where association is

present; the assumption is merely a mathematical convenience. It seems reasonable to assume, for purposes of investigation and in absence of any evidence to the contrary, that if all the more chemical factors, association, ionisation, and solvation, are allowed for, the law will hold for any solution, and that the physical quantities which enter into the thermodynamic equation will be allowed for automatically, since these quantities are undoubtedly functions of the more chemical factors.

Although it is not at present possible to deduce the general laws for lowering of vapour pressure and freezing point, raising of boiling point, etc., we know that these laws are interconnected by a series of rigid thermodynamic differential equations which are independent of concentration, ionisation, association, and solvation, and can therefore be certain that general qualitative conclusions drawn from results obtained by one of these methods can be applied in discussing the results of any of the other methods, whether association, solvation, etc., occur or not.

The vapour pressure law can be deduced for dilute solutions without making any assumption as to the molecular aggregation of either solute or solvent, or as to whether solvation occurs. The only assumption necessary for thermodynamic treatment in this case is that the solution is infinitely dilute.

This method of derivation gives no information as to whether the law applies where association of the solute occurs, since we know as the result of a very large number of experimental determinations that zero association is always indicated at infinite dilution.

As regards solvation, it follows that where this occurs, the solvated complex behaves as a single molecule at infinite dilution, and it is reasonable to assume that in more concentrated solution the law is observed if the quantity of solvent solvated at a given concentration is subtracted from the total solvent.

It also follows from the method of deriving the law for dilute solutions, that in the vapour pressure relation $\dfrac{p-p'}{p} = \dfrac{n}{N+n}$, N, the number of molecules of the solvent, is that corresponding with the normal molecular weight, whatever degree of association the solvent may have in the liquid state.

The evidence that the solution laws hold when association takes place is at present purely experimental, and rests on the formation of definite complexes by organic acids and oximes in a number of solvents.   In the present communication, it is shown that formanilide and acetanilide also form definite complexes.

Benzene as Solvent.

The results obtained with a number of substances which did not show a great departure from Raoult's law are shown graphically in Fig. 1. Determinations belonging to different series on a curve are distinguished by circles, crosses, or dots.

It will be seen that there is a break in several of the curves where the series at lowest concentrations (5—50 per cent.) meets the next series (60—80 per cent.), and is naturally most marked where the curve is approximately straight. The break is obviously due to some form of experimental error in the second series,

FIG. 1.

Percentage concentration for azobenzene.

Percentage molecular concentration 100 $n/N+n$.

I. Formyldiphenylamine.   V. Methyl salicylate.
II. Phenanthrene.   VI. Benzophenone.
III. Benzil.   VII. Azobenzene.
IV. Hexadecyl alcohol.
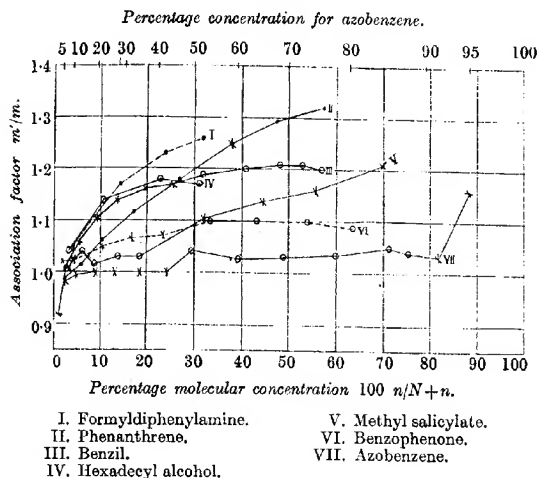
amounting sometimes to from 3 to 4 per cent., and apparently constant throughout the series. The cause of this error is not at all obvious.

One of the substances, azobenzene, obeys Raoult's law absolutely within the limit of experimental error.

All the other substances show more or less association in concentrated solution. From the degree of their abnormality, the general conclusion may be drawn that those groups which cause slight but distinct association in dilute solution of the compounds of lowest molecular weight containing them, also cause a slight association in concentrated solution with compounds of such high

molecular weight that they do not show appreciable association in dilute solution, and, further, that the laws which connect the constitution of the solute with degree of association for the larger abnormalities in dilute solution also apply to the smaller abnormalities in concentrated solution.

Phenanthrene shows slight abnormality by both the cryoscopic and ebullioscopic methods; it is not therefore surprising that it shows distinct association in concentrated solution. The abnormality is, however, of interest, as on general grounds

Fig. 2.

Acids and oximes in benzene at 75°.

Percentage molecular concentration 100 $n/N + n$.

I. Cinnamic acid.   IV. Phenylacetic acid.
II. β-Benzilmonoxime.   V. d-Camphoroxime.
III. Acetophenoneoxime.
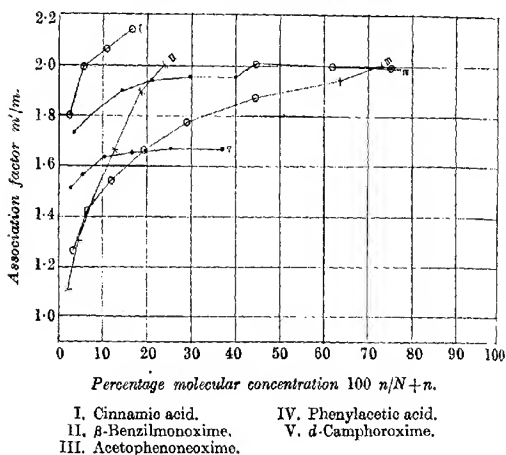
phenanthrene might be expected to form an ideal solution with benzene.

Acids and Oximes.

β-Benzilmonoxime, acetophenoneoxime, and phenylacetic acid all show a maximum association factor of 2. β-Benzilmonoxime was not sufficiently soluble to carry the series further (Fig. 2).

Cinnamic acid shows a decided tendency to give a higher molecular weight than that corresponding with the double formula; it seems probable that this is due to the presence of a double bond in the molecule. The solubility was not sufficient to carry the series further. d-Camphoroxime shows a rapid increase in associa-

tion up to 10 per cent., but only reaches a maximum of 1·66, and has almost this value over a range of 27 per cent. By the cryoscopic method in benzene, association factors approaching 2 are obtained even in 5 per cent. solution. In naphthalene (m. p. 80°), on the other hand, its behaviour is very similar to that in benzene at 75°, and it gave an association factor of 1·6 at a concentration of 10·50 grams per 100 grams of solvent (Innes, *Diss.*, Heidelberg, 1896, p. 42), the highest concentration at which it was examined.

Fig. 3.

Formanilide in benzene.

Percentage molecular concentration 100 $n/N+n$.
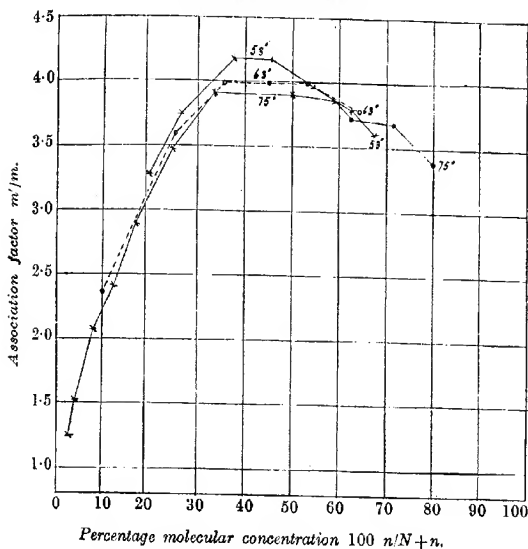
The low maximum would therefore seem to be connected with the temperature at which the determinations were carried out.

Anilides.

The results obtained with formanilide are shown graphically in Fig. 3.

Series of determinations were made at 75°, 63°, and 53°.

The constancy of the association factor over a considerable range concentration at 75° and 63°, as well as the small temperature

effect on the maximum, points to the formation of a definite mole-cular complex containing four simple molecules.

Acetanilide gives a curve at 75° similar to that of formanilide, but the rate of association is still more rapid (Fig. 4).

FIG. 4.

Acetanilide in benzene.
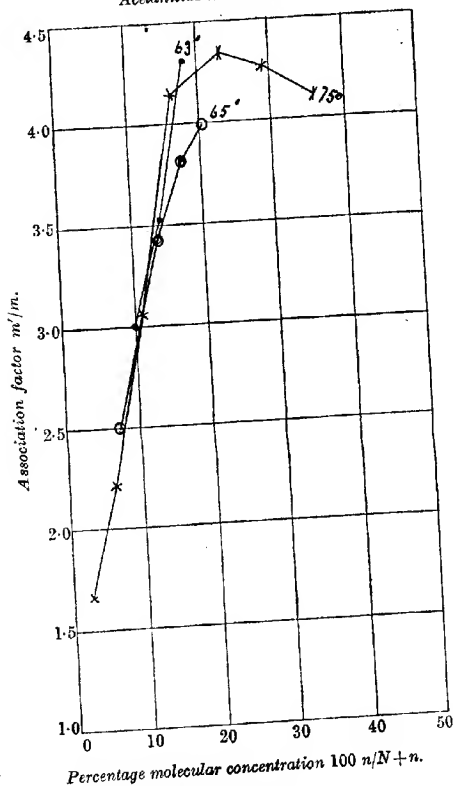
At 63° the solubility is considerably less than at 75°; at both temperatures, the solution of highest concentration is nearly saturated. The series at 63° was repeated at 65°, as a doubt was felt as to whether the whole of the solute was in solution in the last determination at 63°. With the exception of this determina-

tion, the curves at 63° and 65° are either practically identical with that at 75° or below it, indicating an increase of association with increase of temperature.

Since increase of association with increase of temperature is improbable, and the values at 63° and 65° fall well on the same urve, it seems possible that the series at 75° is affected by experimental error.

Taken by themselves, the values obtained with acetanilide do not point to the formation of a definite molecular complex, but . he fact that there is not more difference in the maximum values f acetanilide and formanilide, although the concentrations at which they reach this maximum are so different, does indicate that uch a complex is formed. There seems to be a slight tendency to urther association, as with formanilide at 53°.

Dimethyl Tartrate.

This substance, containing two hydroxyl groups, is extremely abnormal. Its behaviour in dilute solution at different temperatures has already been investigated (Innes, *loc. cit.*). In concentrated solutions, it shows the characteristic alcohol type of curve p to concentrations approaching 50 per cent. molecular, and the nfluence of temperature both on the rate of increase of association and on the maximum association is most striking. There is no evidence of the formation of a definite molecular complex Fig. 5).

The values obtained beyond equimolecular concentration at 63° nd 53° suggest that the molecular weight would be normal at 100 er cent., and that the shapes of the upward and downward curves n each side of equimolecular concentration are either identical part from experimental error) or very similar. Lines of equal ope are shown dotted in the figure. The values obtained at 75° e not consistent with this being the case, but, as has already en pointed out, the probable error in these series, at high concentrations, is much greater than at the lower temperatures.

Ethyl p-Hydroxybenzoate.

This substance, the only abnormal phenol examined, was unfortunately of limited solubility. The first two determinations w a very rapid increase of association, and the line joining them almost linear with the intersection of the co-ordinates. With ease of concentration, the rate of increase of association finishes rapidly, the shape of the curve indicating that a maxi-

mum would be reached with an association factor between 2·8 and 3. As the solubility would be less at lower temperatures, it seemed useless further to examine this substance.

Fig. 5.

Dimethyl tartrate in benzene.

Percentage molecular concentration 100 $n/N+n$.
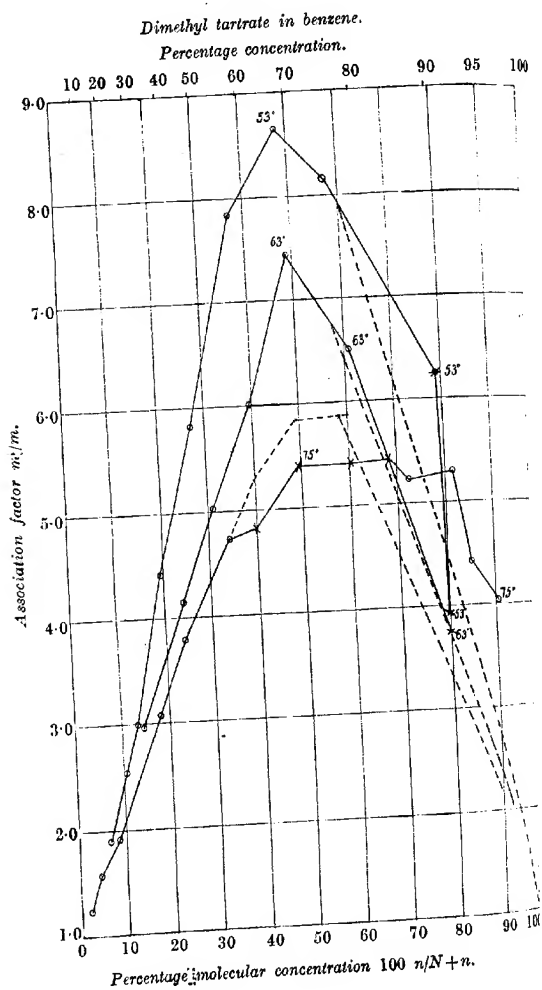
Alcohol as Solvent.

Four substances were examined in alcohol, and all were found to give abnormal molecular weights (Fig. 6).

Phenanthrene and benzil give practically identical molecular

FIG. 6.

Alcohol as solvent.

Molecular concentration 100 $n/N+n$.
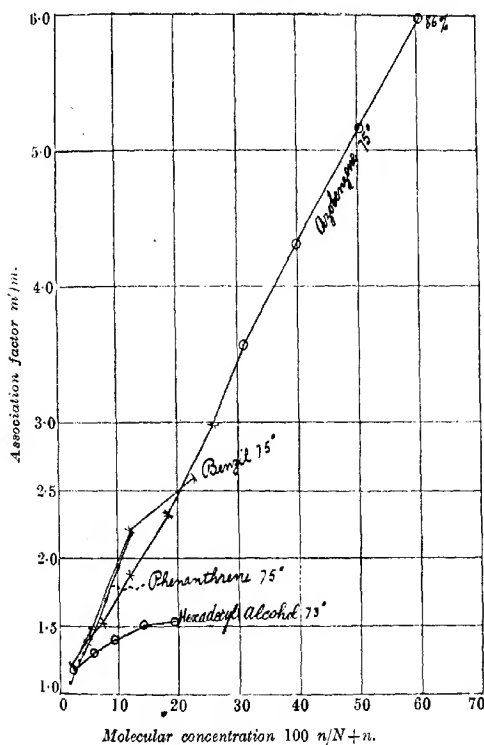
ights at equal molecular concentrations up to the limit of solubility of phenanthrene, and the rate of increase is nearly linear very rapid. The last determination with benzil shows a reasing rate of association.

Azobenzene is also extremely abnormal; it gives values for the molecular weight somewhat smaller than those with benzil and phenanthrene at the same molecular concentration, and the rate of increase is at first slightly less, then slightly greater, than linear. The last four determinations (63·2 to 85·9 per cent.) are exactly linear, and when produced to zero concentration, give the normal molecular weight with considerable accuracy.

Hexadecyl alcohol is about twice as abnormal as in benzene.

The view is very generally held that organic solutes should show less tendency to association in alcohol than in benzene, since the conductivity of electrolytes in benzene is extremely small, whilst in alcohol their conductivity is considerable, and it has been assumed that a substance with dissociating power for electrolytes would not favour the formation of complex molecules. If we admit this view, it might be argued that the abnormalities in alcoholic solution are not due to association. The fact that three substances of such different constitution as azobenzene, phenanthrene, and benzil should all be highly abnormal and to almost the same extent over a considerable range of concentration, whilst in benzene, in concentrated solution, they behave so differently, also suggests that the abnormality is not due to the solute, *per se*, but to some specific action of the solvent. It therefore seems advisable to consider the possible ways in which the solvent could exert an influence on the apparent molecular weight.

That associated liquids, such as alcohol, have an abnormally low vapour pressure has been well established (Vernon, *Chem. News*, 1891, **64**, 54; Young, *Phil. Mag.*, 1892, [v], **34**, 507; T., 1893, **63**, 1251; van't Hoff, "Lectures," Part 3, 50). It is also known that, in solution, alcohol is non-associated at sufficient dilution, whether in an inert or in an associating solvent.

If, therefore, we add to alcohol a miscible, inert, non-volatile liquid, the vapour pressure of the alcohol will not be that corresponding with its molar fraction, but will be larger by an amount which is a function of the dissociation of the complex molecules of the alcohol. An abnormally small lowering of the vapour pressure will therefore be obtained. The effect of the smaller lowering of the vapour pressure will be to increase p' and decrease $p - p'$ in $m = \dfrac{qMp'}{G(p - p')}$, and both these influences will increase the apparent molecular weight. With such an inert solute, in a solvent the liquid molecules of which are associated, but not the vapour molecules, we should expect to get values for the molecular weight of the solute, which point to the normal molecular weight at extreme dilution, and increase with concentration at a rate which is a

function of the dissociation of the complex molecules of the solvent. Hexadecyl alcohol might be expected to be such an inert solute with respect to alcohol, since it appears to be a general rule that substances of constitution similar to that of the solvent give normal molecular weights in that solvent. The departure of hexadecyl alcohol from Raoult's law may therefore be attributed to the progressive dissociation of the alcohol as it is diluted with the hexadecyl alcohol, and the much greater abnormality of the other substances must be sought in some other influence.

When there is combination between the solute and solvent, it is evident that part of the solvent is removed from the solution and no longer functions as solvent. G is therefore decreased, and at the same time p' will be decreased owing to the increased concentration of the solute complex, and $p - p'$ increased. The decrease of G and p' and the increase of $p - p'$ would all act in the direction of decreasing the molecular weight. It is further evident that the influence of such combination will become very great as the concentration approaches $n = N$, provided the compound or complex formed does not exert a decided vapour pressure.

After the experiments described in this paper had been carried out, the apparatus was used by Mr. B. C. Burt, who determined the vapour pressure of concentrated sulphuric acid solutions (T., 1904, **85**, 1345). His results, when suitably plotted (Fig. 7), show in a most striking manner the influence of combination between solute and solvent in molecular weight determinations in concentrated solutions.

Burt determined the vapour pressure of solutions ranging from 25 to 95 per cent., and calculated the molecular weights by Raoult's formula, using Regnault's values for the vapour pressure of water.

The experimental figures at 100° were used when available; at the higher concentrations, it was necessary to take results at higher temperatures. As the influence of temperature at these high concentrations is very small, the form of the curve cannot be seriously affected. The curve of molecular weight against percentage concentration shows the influence of $n = N$ most clearly. There is first a rapid, then a slower fall until $n = N$ is reached, after which the molecular weight is practically constant and almost zero.

Since, in a solution in which the solute is practically non-volatile and the solvent readily volatile, any chemical compound formed must have a much smaller vapour pressure than that of the solvent, it is evident that, in such solution, combination between solvent and solute cannot occur if the normal or a high molecular weight is indicated at or near equimolecular concentration.

Since neither the dissociation of the solvent nor combination

between solute and solvent will explain the great abnormality of phenanthrene, benzophenone, and azobenzene in alcohol, it can only be supposed that the abnormality is due to association, and it follows *that alcohols and the "associating solvents" exert an associating influence on each other.*

Alcohol was first used as an ebullioscopic solvent by Beckmann (*Zeitsch. physikal. Chem.*, 1890, **6**, 454), and from his results in this and other solvents, he drew the conclusion that solvents like the alcohols, organic acids, and phenols, containing hydroxyl groups, are "dissociating solvents of the water type," and consequently complex molecules are not formed in them. Nernst lent support to Beckmann's hypothesis, by the theory that the higher

FIG. 7.

Apparent molecular weight of sulphuric acid (1) *against molecular concentration,* (2) *against percentage concentration.*
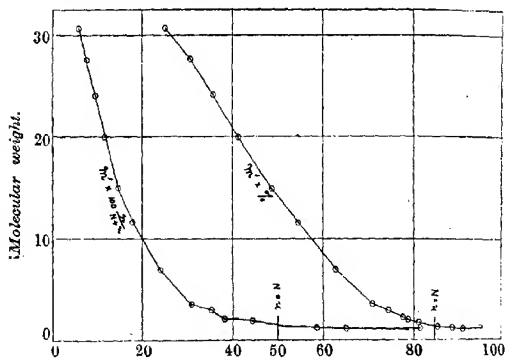
the dielectric constant of a solvent, the greater will be its power to split up double molecules.

It is of interest to examine the experimental results on which Beckmann founded his theory. These are shown graphically in Fig. 8 for alcoholic solutions, molecular weights being plotted against concentration. Carbamide and racemic acid have not been included, the former because it was only examined in dilute solution, the latter because the values are irregular.

A glance at the curves will show that, with the exception of the acids, all the substances show a much more rapid increase of molecular weight than is shown by "normal" substances in benzene or naphthalene. Benzil, phenyl benzoate, ethyl benzoate,

and naphthalene, substances belonging to the "associating type" of solvent, are very abnormal; borneol, acetophenoneoxime, and acetanilide, belonging to the "water type," are less abnormal, and the curves of the last three substances are approximately parallel. If the view already brought forward, that the abnormality of hydroxy-compounds in alcohol is due to the dissociation of the

FIG. 8.

Beckmann's results in alcohol by the ebullioscopic method.

Grams of solute per 100 grams of solvent.

I. Benzil, 210.
II. Phenyl benzoate, 198.
III. Ethyl benzoate, 150.
IV. Borneol, 154.
V. Naphthalene, 128.
VI. Acetanilide, 135.
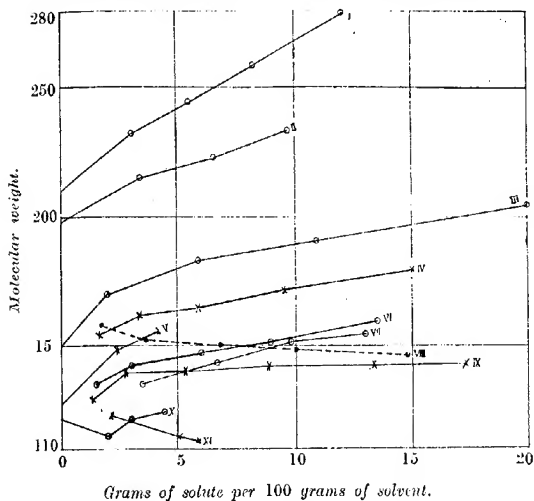
VII. Acetophenoneoxime, 135.
VIII. Tartaric acid, 150.
IX. Salicylic acid, 138.
X. Benzoic acid, 122.
XI. Succinic acid, 118.

alcohol complex, is correct, these curves should be parallel for equal molecular concentrations.

Succinic and tartaric acids show a decreasing molecular weight with concentration; evidently this is due to ester formation and combination of the water formed with the solvent. The normal molecular weights with salicylic acid must be attributed to a balance between the abnormality due to the dissociation of the solvent and that due to ester formation.

Beckmann's results therefore lend strong support to the deduc-
tion that there is mutual association between alcohols and sub-
stances of the hydrocarbon type.

Beckmann's classification into two types is still useful, however,
and it is proposed to call the "associating solvent" type of sub-
stance *Carbotype*, and the "water type" of substance *Oxytype*,
without, however, assuming any sharp line of demarcation between
the two classes.

Numerous instances have been published of the comparatively
normal behaviour of hydroxylated compounds and anilides in ethyl
and methyl alcohols, but very few instances of association in
alcohol, apart from those in Beckmann's paper, appear to have
been observed. The following have been found (Peddle and
Turner, T., 1911, **109**, 696):

m-Dinitrobenzene, $2·6—5·5$, $1/100$ gram-mols, per 100 c.c.,
$m' = 181—211$, $m = 168$.

Diphenylamine, $3·79—5·99$, $1/100$ gram-mols. per 100 c.c.,
$m' = 190—206$, $m = 169$.

Phenanthrene, $1·94—11·99$ grams per 100 grams of solvent,
$m' = 183—226$ (Behrend, *Zeitsch. physikal. Chem.*, 1892, **10**, 279).

Numerous salts, inorganic and organic, have been examined
ebullioscopically in alcohol, and many of these show association as
well as the influence of combination with the solvent (Turner and
Pollard, T., 1914, **105**, 1751).

The close similarity in behaviour between the alcohols and
phenols in solvents of the hydrocarbon type suggests that phenols
and carbotype substances should also show mutual association.
Robertson (T., 1906, **89**, 567) has shown that the hydrocarbons are
highly associated in phenol solution, also that carbon tetrachloride
is as abnormal as the hydrocarbons.   Ethylene dibromide and
bromoform are also abnormal, but to a less extent.   The mutual
association of the abnormal phenols and substances of the carbo-
type group must therefore be considered to be a general
phenomenon.

The degree of abnormality of the substituted phenols follows
definite laws as regards the nature and position of the substituting
group, and the anilides follow similar laws.   There seems little
doubt, therefore, that a carbotype solute will give abnormal mole-
cular weights in an anilide, and that mutual association takes
place in this case also.   Anilides do not seem to have been used as
cryoscopic solvents, although formanilide (m. p. 46°) would be a
convenient substance to use.

If mutual association takes place with acids and oximes in a
carbotype solvent, it is obvious that no direct evidence of this

being the case can be obtained from the behaviour of a carbotype solute in an acid or oxime if the acid or oxime is associated to a double molecule in the liquid state.

There is, however, evidence that during the association of an acid or oxime in a carbotype solvent, the solvent exerts a specific influence on the association of a nature which has not been explained. If the solvent merely acted as a diluent, the mass law should apply to the dissociation of the double molecules, as in gaseous dissociation. Auwers (Zeitsch. physikal. Chem., 1907, **60**, 385) has shown that with acids and oximes this is by no means the case, C_1^2/C decreasing very rapidly with concentration.

The data obtained in the present investigation are more suitable for such calculations than those used by Auwers, since the determinations were made isothermally; the results of calculation are, however, similar. The anilides also show large variations in the value of C_1^4/C.

Since there is direct and fairly conclusive evidence of mutual association between alcohols and phenols and a carbotype, it is reasonable to ascribe the influence of the carbotype solvent on the association of the acids, oximes, and anilides to the same cause.

The position of the maximum association of dimethyl tartrate in benzene at or near equimolecular concentration evidently indicates that in this instance association of solute and solvent takes place at the same rate. Although there is no evidence as to the rate of association of the solvent in other instances, it is not unreasonable to assume, for purposes of further investigation, that in a solvent which is non-associated in the liquid state, association of solvent and solute is in general equal.

The cause of mutual association of solute and solvent obviously cannot be chemical, as anything in the nature of combination between the two constituents, in concentrated solution, is impossible (p. 425). The only adequate explanation which has occurred to the author is that it is electrical in character.* It seems reasonable to suppose that the association begins in the oxytype substance, whether this is functioning as solvent or solute. If we imagine that for each molecule entering into an aggregate a definite quantity of electricity passes to the carbotype substance, causing in it an association equal to that in the oxytype, and that this goes on until an equilibrium is attained, depending on the temperature, concentration, pressure, and nature of the solvent and solute, this would account for the fact that dimethyl tartrate and benzene appear to associate at the same rate.

* That association may be due to electrical, not chemical, forces has already been suggested by Turner and English (T., 1914, **105**, 1793).

If we assume that the charge that passes when a substance associates is one electron per molecule, the charge per aggregate must be considerable when the association reaches 6—10, as with dimethyl tartrate. It might therefore be supposed that the molecules would arrange themselves in a definite geometric arrangement depending on their mutual attractions and repulsions, and that they would resist any influence which tended to alter this arrangement. The high viscosity of associated solutions would thus be explained.

Benzene as Solvent.

Azobenzene, $C_{12}H_{10}N_2 = 182.$

t	p	$p-p'$	G	g	Per cent.	$\dfrac{100\,n/}{N+n.}$	m'	$m'/m.$
75°	64·98	1·69	17·8	1·059	5·72	2·54	178	0·978
		3·34		2·193	11·2	5·12	181	0·995
		6·05		4·185	19·3	9·28	182·5	1·002
		8·72		6·30	26·6	13·3	182·5	1·002
		11·98		9·19	34·55	18·5	182	1·000
		15·78		13·02	42·9	24·2	182	1·000
75	65·09	18·89	8·9	8·54	49·7	29·8	189	1·042
		25·12		12·98	60·1	39·3	187	1·026
		31·30		19·18	69·0	49·0	188	1·030
		38·19		29·52	77·4	59·6	188	1·035
		45·69		49·56	85·2	71·3	191	1·050
		48·49		60·78	87·6	75·2	189	1·039
75	65·10	56·94	2·66	44·72	95·0	88·2	212	1·16
		53·3	4·435		91·8	82·1	187	1·03
		48·15	7·10		88·6	73·5	181	0·995

Benzophenone, $C_{13}H_{10}O = 182.$

t	p	$p-p'$	G	g	Per cent.	$\dfrac{100\,n/}{N+n.}$	m'	$m'/m.$
72°	58·84	1·27	22·19	1·144	4·98	2·20	185·5	1·02
		3·62		3·422	13·56	4·54	186	1·02
		6·23		6·321	22·4	11·03	191	1·05
		9·49		10·42	32·3	17·0	194	1·065
		12·95		15·52	41·7	23·4	195	1·07
75	65·18	20·27	8·90	9·98	53·6	33·3	200	1·10
		26·55		15·17	63·7	43·1	200	1·10
		33·36		23·25	73·0	53·9	201	1·10
		40·07		34·95	80·4	63·5	198	1·09

Benzil, $C_{14}H_{10}O_2 = 210.$

t	p	$p-p'$	G	g	Per cent.	$\dfrac{100\,n/}{N+n.}$	m'	$m'/m.$
75	65·02	0·59	22·19	0·567	2·53	0·955	202	0·92
		1·72		1·622	6·94	2·68	213	1·013
		3·46		3·517	13·9	5·65	224	1·067
		5·68		6·18	22·0	9·52	232	1·105
		8·04		9·38	30·0	13·7	239	1·140
		11·35		14·43	40·9	20·1	244	1·16
		14·80		20·27	48·2	25·6	246	1·17
75	65·17	18·53	8·90	10·94	56·1	32·0	250	1·19
		23·85		16·06	65·2	41·0	252	1·20
		28·22		21·42	69·2	48·1	254	1·21
		31·57		26·32	75·2	53·1	254	1·21
		34·27		30·88	78·3	57·1	522	1·20

Benzene as Solvent—(continued).

Formyldiphenylamine, $C_{13}H_{11}ON = 197$.

t	p	$p-p'$	G	g	Per cent.	$\dfrac{100\,n}{N+n}$	m'.	m'/m
75	65·21	1·46	17·8	1·015	5·51	2·26	198	1·005
		2·72		2·017	10·40	4·39	208	1·05
		5·21		4·229	19·6	8·81	218	1·105
		8·35		7·562	30·2	14·73	230·5	1·17
		12·41		12·69	42·1	24·25	242	1·23
		17·76		20·79	54·5	32·2	249	1·26

Methyl Salicylate, $C_8H_8O_3 = 152$.

t	p	$p-p'$	G	g	Per cent.	$\dfrac{100\,n}{N+n}$	m'.	m'/m
75	64·90	1·71	22·19	1·176	5·10	2·69	153	1·005
		4·05		2·944	11·92	6·49	158	1·04
		5·65		4·171	16·06	8·94	155	1·015
		8·81		6·871	23·9	13·9	156·5	1·03
		11·70		9·822	31·05	18·7	160	1·05
75	65·18	42·85	4·45	18·83	82·1	70·0	185	1·21
		33·81	8·01		71·1	55·6	177	1·16
		26·89	12·46		60·9	44·4	174	1·14
		21·8	17·8		52·0	32·4	168	1·105

Phenanthrene, $C_{14}H_{10} = 178$.

t	p	$p-p'$	G	g	Per cent.	$\dfrac{100\,n}{N+n}$	m'.	m'/m
75	65·13	1·74	22·19	1·340	5·80	2·62	175	0·984
		3·94		3·242	12·95	6·11	180·5	1·101
		6·62		6·002	21·6	10·8	189	1·060
		10·39		10·57	32·6	17·5	199	1·118
		15·61		18·63	46·2	27·2	211	1·18
75	65·14	21·18	8·90	11·82	58·0	37·8	223	1·25
		26·62		17·56	67·3	47·3	230	1·29
		32·98		26·59	73·5	57·6	235	1·32

Hexadecyl Alcohol, $C_{16}H_{34}O = 242$.

t	p	$p-p'$	G	g	Per cent.	$\dfrac{100\,n}{N+n}$	m'.	m'/m
75	65·24	1·09	22·2	1·029	4·50	1·49	217	0·90
		2·04		2·261	9·40	3·24	251	1·04
		4·19		5·008	18·7	6·87	260	1·07
		6·34		8·30	27·6	10·92	276	1·14
		9·58		13·38	38·0	16·5	278	1·15
		13·24		20·245	47·1	23·0	285	1·18
		18·06		30·23	58·2	30·9	284	1·17

Cinnamic Acid, $C_9H_8O_2 = 148$.

t	p	$p-p'$	G	g	Per cent.	$\dfrac{100\,n}{N+n}$	m'.	m'/m
75	64·94	1·07	17·8	0·999	5·73	2·94	263	1·78
		1·96		2·024	10·43	5·77	291	1·965
		3·66		4·074	18·95	11·0	306	2·06
		5·92		7·10	28·95	16·5	316	2·14

Benzene as Solvent—(continued).

Phenylacetic Acid, $C_8H_8O_2 = 136$.

t	p	$p-p'$	G	q	Per cent.	$\frac{100\,n}{N+n}$	m'	m'/m
75	65·26	1·29	17·8	1·059	5·73	3·36	236	1·73
		2·62		2·274	11·54	6·95	244	1·79
		5·23		5·032	22·4	14·2	258	1·90
		7·94		8·13	31·8	21·1	263	1·935
		11·79		13·07	42·8	30·0	265	1·95
		16·57		20·08	53·6	39·8	265	1·95
75	65·51	18·56	8·9	12·06	58·5	44·8	280	2·06
		29·74		24·53	74·2	62·0	270	1·99
		40·23		44·86	84·0	75·2	259	1·90

Acetophenoneoxime, $C_8H_9ON = 135$.

t	p	$p-p'$	G	q	Per cent.	$\frac{100\,n}{N+n}$	m'	m'/m
75	65·12	1·70	17·8	1·013	5·50	3·26	169·6	1·26
		3·09		2·127	10·91	6·60	192	1·42
		5·33		4·132	19·2	12·04	208	1·54
		8·19		7·174	29·2	19·25	224	1·66
		12·15		12·21	41·2	28·9	239	1·77
		19·43		23·92	57·9	44·4	252	1·87
75	65·20	37·5	4·43	19·31	82·4	72·9	269	1·99
		31·15	6·65		75·4	63·8	261	1·94

γ-Benzilmonoxime, $C_{14}H_{11}O_2N = 225$; m. p. 113—114°.

t	p	$p-p'$	G	q	Per cent.	$\frac{100\,n}{N+n}$	m'	m'/m
75	65·30	1·16	17·8	1·046	5·69	2·03	259	1·15
		2·09		2·167	11·11	4·15	295	1·31
		3·62		4·36	20·0	8·00	333	1·475
		5·20		7·34	29·7	12·71	397	1·68
		7·13		11·63	40·1	18·72	425	1·89
		8·87		15·81	47·6	23·98	450	2·00

l-d-Camphoroxime, $C_{10}H_{17}ON = 167$.

t	p	$p-p'$	G	q	Per cent.	$\frac{100\,n}{N+n}$	m'	m'/m
75	65·16	1·22	17·8	1·072	5·80	2·80	252	1·51
		2·29		2·125	10·90	5·40	261	1·58
		4·33		4·316	19·9	10·4	272	1·63
		6·96		7·375	29·7	16·5	276	1·65
		10·99		12·54	41·9	25·2	278	1·66
		17·33		21·96	55·6	37·2	272	1·625

Formanilide, $C_7H_7ON = 121$.

t	p	$p-p'$	G	q	Per cent.	$\frac{100\,n}{N+n}$	m'	m'/m
75	65·20	1·21	22·19	0·795	3·51	2·28	150·5	1·245
		1·78		1·482	6·36	4·19	189	1·562
		2·73		3·014	12·12	8·19	247	2·04
		3·63		4·812	18·1	12·45	293	2·42
		4·28		6·897	24·0	16·93	353	2·91
		5·60		10·99	33·5	24·43	422	3·48
		7·41		17·03	43·9	33·4	475	3·93
		10·39		25·02	54·6	50·3	473	3·91
		14·10		35·99	62·3	58·9	466	3·86

Benzene as Solvent—(continued).

Formanilide, $C_7H_7ON = 121$—(continued).

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'.	m'/m.
75	65·14	11·71	8·90	10·98	56·1	45·1	454	3·74
		15·64		15·82	64·8	54·1	454	3·74
		19·88		21·92	71·8	62·3	250	3·72
		26·85		33·05	79·5	71·4	428	3·53
		35·23		53·23	86·3	80·0	410	3·38
63	43·53	1·87	13·3	2·137	14·1	9·58	288	2·36
		3·74		6·817	34·4	25·25	436	3·60
		5·33		11·14	46·3	35·5	479	3·96
		7·41		16·65	56·2	45·2	486	4·02
		9·70		22·75	63·7	52·9	476	3·94
		14·19		36·87	73·7	64·6	458	3·78
53	30·28	2·10	13·3	4·924	27·4	19·6	396	3·27
		2·62		7·130	35·4	26·1	451	3·74
		3·78		12·07	48·0	37·4	508	4·13
		5·07		16·92	56·6	45·6	505	4·18
		6·99		23·97	64·9	54·4	480	3·96
		9·27		33·65	72·2	62·7	458	3·79
		11·05		41·64	76·4	67·4	435	3·60

Acetanilide, $C_8H_9ON = 135$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'.	m'/m.
75	64·96	1·36	17·8	1·070	5·76	2·43	224	1·66
		1·83		1·931	10·0	6·03	299	2·21
		2·45		3·628	17·2	10·8	414	3·06
		2·86		5·79	24·9	16·1	563	4·17
		4·20		9·05	34·2	23·1	586	4·34
		5·73		12·45	41·7	29·2	576	4·26
		7·87		17·18	49·7	36·2	557	4·12
63	43·60	1·55	22·2	4·18	16·0	9·93	404	2·99
		1·94		6·23	22·2	14·1	480	3·55
		2·16		8·43	27·8	18·2	580	4·30
65	46·58	1·39	22·2	3·041	12·2	7·41	354	2·62
		2·04		5·895	21·2	13·40	461	3·42
		2·48		7·96	26·6	17·45	507	3·76
		2·92		9·95	31·2	20·6	532	3·95

Dimethyl Tartrate, $C_6H_{10}O_6 = 178$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'.	m'/m.
75	64·97	1·08	17·8	0·853	4·66	2·1	226	1·22
		1·97		1·829	9·54	4·62	262	1·47
		2·97		3·524	14·7	8·15	342	1·92
		3·69		5·94	25·4	13·03	441	2·48
		4·33		8·78	33·5	18·1	550	3·08
		4·99		12·59	41·9	24·0	677	3·80
		6·57		20·78	54·5	34·3	826	4·64
75	65·20	6·59	8·90	8·50	49·7	30·4	687	3·86
		7·82		12·92	60·0	39·8	860	4·82
		10·00		19·27	69·1	49·6	966	5·43
		14·3		29·89	77·6	60·5	966	5·42
		18·41		42·32	83·2	68·5	976	5·49

Benzene as Solvent—(continued).

Dimethyl Tartrate, $C_6H_{10}O_6 = 178$—(continued).

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n.$	$m'.$	$m'/m.$
75	65·18	46·25	2·76	55·71	95·8	90·9	725	4·07
		36·67	4·54		92·9	85·2	796	4·47
		30·06	5·85		91·2	81·8	930	5·22
		20·83	9·70		85·8	72·4	995	5·60
63	43·63	2·56	13·3	5·443	29·5	15·5	524	2·94
		3·09		9·37	41·8	23·9	739	4·15
		3·56		13·22	50·5	30·8	895	5·02
		4·16		19·27	59·6	39·4	1099	6·17
		4·92		28·08	68·4	48·6	1324	7·44
		8·47		46·42	78·3	61·0	1155	6·50
63	43·53	24·53	4·43	45·35	91·5	80·3	664	3·72
53	30·23	1·04	13·3	2·053	13·4	6·47	338	1·89
		1·31		3·416	20·8	10·3	452	2·54
		1·53		4·69	26·4	13·6	528	2·97
		1·56		7·14	35·4	19·3	788	4·42
		1·81		11·00	45·8	26·9	1038	5·83
		2·07		17·09	56·7	36·5	1395	7·84
		2·88		26·07	66·8	46·9	1540	8·66
		4·23		39·4	75·2	57·1	1453	8·16
53	30·2	11·4	6·65	54·46	89·6	79·1	1113	6·25
53	30·2	15·4	6·21	54·68	90·3	80·2	694	3·9

Ethyl p-Hydroxybenzoate, $C_9H_{10}O_3 = 166$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n.$	$m'.$	$m'/m.$
75	65·16	1·18	17·8	0·900	4·91	2·38	219	1·32
		1·97		2·017	10·4	5·17	290	1·75
		3·21		4·299	19·8	10·4	372	2·24
		4·70		7·48	30·0	16·8	430	2·59
		7·10		12·47	41·7	25·2	455	2·74

Alcohol as Solvent.

Hexadecyl Alcohol, $C_{16}H_{24}O = 242$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n.$	$m'.$	$m'/m.$
73	61·90	1·39	15·78	2·114	12·1	2·54	276	1·14
		2·80		4·995	24·5	5·82	316	1·30
		4·23		8·25	34·8	9·26	347	1·43
		6·14		13·43	46·7	14·3	365	1·51
		8·43		19·60	56·0	19·5	372	1·54

Benzil, $C_{14}H_{10}O_2 = 210$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n.$	$m'.$	$m'/m.$
75	66·85	0·54	19·72	0·893	4·41	0·98	261	1·24
		1·21		2·023	9·50	2·20	261	1·24
		2·57		5·352	21·6	5·61	316	1·505
		4·02		12·42	39·2	12·12	462	2·20
		5·38		20·01	50·9	22·4	544	2·59

Alcohol as Solvent —(continued).

Phenanthrene, $C_{14}H_{10} = 178.$

t	p	$p-p'$	G	g	Per cent.	$100\,n/$ $N+n.$	m'.	$m'/m.$
75	66·91	1·10	15·78	1·105	6·70	1·82	198	1·11
		2·15		2·483	13·87	4·01	224	1·26
		3·00		4·399	22·2	6·89	279	1·57
		3·92		7·65	33·1	11·4	368	2·06
75	66·97	0·90	19·72	1·033	5·09	1·36	181	1·016
		1·19		1·462	7·03	1·92	190	1·07
		1·87		2·667	12·12	3·45	222	1·247
		2·75		4·537	19·06	5·71	252	1·42
		3·28		6·54	25·3	8·02	303	1·70
		3·59		8·192	29·8	9·88	344	1·93
		4·03		10·40	35·0	12·20	368	2·17

Azobenzene, $C_{12}H_{10}N_2 = 182.$

t	p	$p-p'$	G	g	Per cent.	$100\,n/$ $N+n.$	m'.	$m'/m.$
75	67·15	1·26	15·78	1·356	8·69	2·18	212	1·165
		2·36		2·881	15·8	4·52	236	1·30
		3·47		5·029	24·6	7·63	276	1·52
		4·56		8·30	35·0	12·0	342	1·88
		5·70		13·08	46·0	17·8	421	2·31
		6·88		20·60	57·2	25·3	550	2·96
75	67·15	7·35	7·89	12·95	63·2	30·4	647	3·56
		8·90		19·45	72·3	39·6	781	4·29
		10·98		29·84	80·1	50·2	939	5·16
		13·63		45·05	85·9	60·2	1083	5·96

The experiments described in this paper were made in the Chemical Laboratories of the University of Liverpool and the Harris Institute, Preston. The author wishes to express his indebtedness to the late Dr. J. C. Brown for supplying a dividing engine and several chemicals, and to Dr. P. F. Frankland for the loan of the electromagnetic stopcock.

XXXVI.—*The State of Potassium Oleate and of Oleic Acid in Solution in Dry Alcohol.*

By MARY EVELYN LAING.

EVER since Krafft's second paper (Krafft, *Ber.*, 1899, **32**, 1584; compare Krafft and Strutz, *Ber.*, 1896, **29**, 1328) on the molecular weights of the salts of the higher fatty acids in dry alcohol, soap has served as the typical instance of a substance which is a crystal-

S*

loid of normal molecular weight in alcohol, although in water it is a colloidal electrolyte.* This conception and definition of colloidal electrolytes to which the six years' study of soap solutions in this laboratory up to 1914 has led, made it appear possible that in alcohol also the apparent simplicity of Kráfft's last result was illusory and that, as in some aqueous solutions, extensive dissocia tion and formation of colloid might occur, the more so since his previous paper had indicated that in absolute alcohol soap existed in the form of double molecules. For this reason, the molecular weight in alcohol has been redetermined. Further, the electrical conductivity has been measured in order to ascertain whether the ionisation is great or negligible.

Potassium oleate was chosen for study because of its ready solu bility in alcohol, since in many cases the formation of colloid or colloidal electrolyte is only appreciable in high concentration. Its solutions are never devoid of opalescence, and they have a distinct tendency to froth.

The result has been to show that potassium oleate both in anhydrous and in moist ethyl alcohol is essentially a simple electro lyte dissociating to a very moderate extent into simple ions. Only quite small amounts of colloid can be present.

Solutions of oleic acid, which also froth readily and for which no ebullioscopic data existed, were likewise investigated, particu larly as Dennhardt (Diss., 1898; Ann. Phys. Chem., 1899, [iii], 67, 325) had obtained conducting curves in methyl and ethyl alcohols, exhibiting in each case a pronounced maximum and minimum. Such phenomena are of very frequent occurrence in the literature of non-aqueous solutions, and in certain cases their explanation appears to me to offer great difficulties.

The results have shown that Dennhardt's data are quite untrust worthy (for other evidence, see below), and that oleic acid also, in all concentrations, is a simple electrolyte, only very slightly dis sociated. Consequently, the theoretical difficulties of interpreta tion vanish, and it seems quite possible that a number of other similar cases may also be due to experimental error.

EXPERIMENTAL.

Dry ethyl alcohol was prepared from absolute alcohol which had been kept over specially burnt quicklime for three years; during

---

* " Colloidal electrolytes are salts in which one ion has been replaced by a heavily hydrated micelle that conducts electricity just as well or even better and carries an equivalent sum total of electrical charges." (See McBain, *Trans. Faraday Soc.*, 1913, **9**, 99. *Kolloid Zeitsch.*, 1913, **13**, 56; T., 1914, **105**, 957, and McBain and Salmon, *J. Amer. Chem. Soc.*, 1918.

this time, the liquid had become a soft, pale yellow jelly owing to the formation of calcium ethoxide. The alcohol was distilled from this material and preserved with the usual precautions. Three separate specimens were used, and identical results obtained in molecular weight determinations. It had D_4^{15} 0·7925, a value only 0·1 per cent. too low, indicating, presumably, the presence of a small amount of ether (water would affect the density in the opposite direction).

All vessels and instruments were carefully calibrated, and the precautions described in earlier papers from this laboratory observed. The oleic acid used was colourless, almost odourless, melting at 9·0°, and having D_4^{18} 0·8938.

Dry potassium oleate was prepared in the following manner. Potassium balls were cleaned by washing with several changes of methylated ether; the balls were at once wiped with filter paper and dropped into dry alcohol. Finally, oleic acid was added to the potassium ethoxide until a sample diluted with about one-quarter of its weight of water (previously boiled) gave a neutral reaction towards phenolphthalein. The solution was then evaporated under diminished pressure over calcium chloride, the potassium oleate being left as a soft, pure white powder.

Molecular Weight of Potassium Oleate in Anhydrous and Moist Alcohol.

Beckmann's ordinary apparatus was employed. Concentrations are expressed in mols. per 1000 grams of alcohol (weight normality).

Concentration.	Grams per 100 grams of alcohol.	Rise in boiling point.	Molecular weight.
0·14	4·518	0·173°	303·4
0·32	10·21	0·388	302·4
0·44	14·09	0·528	306·7
0·49	15·71	0·590	306·1
0·54	17·34	0·654	305·2
0·63	20·16	0·764	303·2
0·70	22·32	0·820	305·6
0·84	26·91	1·008	306·9
0·91	29·18	1·100	305·2
1·00	32·04	1·238	297·9
1·14	36·80	1·350	311·6
		Mean	304·9
		Theory	320·5

The experiments comprise a number of independent series extending up to fully saturated solution. The results show no tendency for the molecular weight to alter with concentration, and they give data rather smaller than that required for the simple molecular weight. This is explained by the moderate dissociation measured below. The value here obtained agrees substantially

s* 2

with that which Krafft himself found in his second paper, namely, 347, instead of twice the molecular weight.

On the addition of 1, 2, 3, and 4 per cent. of water to the solution, only a very slight alteration in the molecular magnitude was observed, the soap still having a simple molecular weight instead of the larger numbers, namely, 599 to 670, obtained by Krafft and Strutz in their first paper, which appear to be erroneous (see below).

Only the data for the addition of 3·8 per cent. of water (by weight) to the solvent need be presented.

Concentration.	Grams per 100 grams of alcohol.	Rise in boiling point.	Molecular weight.
0·205	6·697	0·243°	311·9
0·278	8·978	0·330	309·7
0·339	10·86	0·400	311·1
0·463	14·84	0·540	315·7
		Mean ...	311·9
		Theory ...	320·5

Krafft considered that his own experiment had confirmed his earlier work with Strutz, for, on the addition of 1·5 c.c. of water to the boiling alcoholic solution, the boiling point was depressed by 0·09°. He appears to have overlooked the fact that a mixture of alcohol and water, containing 96 per cent. of the former, gives a minimum constant-boiling mixture, and therefore the addition of 4 per cent. of water will lower the boiling point of dry alcohol or any solution made from it by about 0·126°. Krafft's experiment, then, if properly calculated, corroborates that just described, and consequently this earlier work is disproved.

Conductivity of Potassium Oleate in Dry Alcohol.

Closed cells of borosilicate glass were employed. The solutions were either made up in the cell by weighing in the constituents or they were made up ad hoc and immediately introduced for measurement.

A preliminary experiment on a nearly saturated solution at 18° gave a molecular conductivity of 1·01 mhos. This solution contained 0·1990 gram of potassium oleate in 16·10 grams of alcohol, and therefore its weight-normality was 0·385N, or nearly 0·3N by volume.

The significance of this result depends on the value of the conductivity, at infinite dilution, in alcohol, which is generally accepted as being one-third of the value in aqueous solution. This leads to a value for α, the degree of ionisation, of 3 per cent.

The solubility increases rapidly on heating, and since it is

impossible to predict the behaviour of non-aqueous solutions on further concentration, the remaining measurements were carried out at 40° and 60°. These are given in table I.

TABLE I.

Conductivity of Potassium Oleate in Ethyl Alcohol at 60°.

Weight normality.	Volume normality.	Density.	Specific conductivity.	Molecular conductivity.
1·14	0·68	0·8220	0·001927	2·806
0·76	0·49	0·8030	0·001812	3·679
0·57	0·38	0·7920	0·001694	4·421
0·46	0·31	0·7850	0·001566	5·045
0·38	0·27	0·7800	0·001452	5·483
0·30	0·22	0·7750	0·001285	5·948
0·23	0·16	0·7705	0·001187	7·053
0·14	0·11	0·7640	0·000891	10·64
0·03	0·02	0·7565	0·000381	19·20

Conductivity at 40°.

0·57	0·39	0·8013	0·001477	3·799
0·46	0·32	0·7961	0·001372	4·359
0·38	0·27	0·7922	0·001291	4·800
0·30	0·22	0·7884	0·001734	5·182
0·23	0·17	0·7848	0·001031	6·160
0·14	0·11	0·7810	0·0008143	7·567
0·03	0·026	0·7755	0·0003420	13·43

The determinations of the densities of the concentrated solutions were not easy, since the solutions frothed readily and on slight cooling solidified in the form of a curd. For these, the arms of the pyknometer were made vertical, with the mark on one just opposite the tip of the other. Around the latter a glass mantle was fitted by means of a loose cork, and the solution was protected from the cork by a thin layer of clean mercury. During the adjustment, this reservoir was raised, so that the open tip of the pyknometer was immersed in the soap solution. As soon as the adjustment to the mark had been made, the reservoir was lowered and emptied, leaving the pyknometer exactly full and completely immersed in the thermostat.

The density is nearly, although not quite, proportional to the concentration. In the case of oleic acid, the divergence from a straight line is slightly greater.

It is seen from the above tables that the conductivity at 60° rises steadily from 2·81 mhos for a 1·14.N(weight)-solution up to the fairly large value of 19·2 for a 0·03.N(weight)-solution, without exhibiting any irregularities.

Since the conductivity at infinite dilution at 60° probably lies between 50 and 60 mhos., the dissociation evidently rises from a value of about 3 per cent. in N-solution to about 30 per cent. in

0·03N-solution. In every case, then, practically all the soap is in crystalloidal form, although, no doubt, a very small amount of colloid must be present.

Oleic Acid in Dry Alcohol.

Oleic acid is a typical case of a substance giving anomalous data in non-aqueous solution, consequently its molecular weight by the ebullioscopic method was first studied.

The results of several series of determinations may be summarised as follows.

From 0·2898 gram to 6·914 grams of acid were dissolved in 12·96 grams to 13·33 grams of alcohol, giving solutions which were 0·07, 0·08, 0·1, 0·26, 0·3, 0·56, 0·60, 0·80, 0·97, and 1·8N(weight), and from the rise in boiling point the following molecular weights are calculated: 297·2, 283·1, 273·6, 270·5, 284·0, 276·0, 294·2, 298·5, 288·1, and 306·9. Mean, 287·1; Calc., 282·3. Difference, 1·7 per cent. There is therefore no doubt with regard to the simple value for the molecular weight or to its constancy over this very great range of concentration. There is clearly also very little dissociation.

We possess very little or no information with regard to the molecular weight of higher fatty acids in water on account of their insolubility in this medium. In quinoline, however, Gabel (*Diss.*, Magdeburg, 1906) found that stearic acid had simple molecular weight, although sodium stearate and palmitate were shown to be colloids.

The next step was to redetermine the conductivity of oleic acid in alcohol. This was measured only at 60°, and the results are given in table II. Every point was determined several times with

TABLE II.

Conductivity of Oleic Acid in Dry Alcohol at 60°.

Weight normality.	Volume normality.	Density.	Specific conductivity.	Molecular conductivity.	$\mu/\sqrt{v} \times 10^{-4}$.	$\mu/\sqrt{v} \times 10^{-}$ corrected
3·64	1·536	0·8368	$1·57 \times 10^{-6}$	$3·58 \times 10^{-3}$	0·24	0·16
1·81	0·955	0·7961	4·01 ,,	4·20 ,,	1·30	1·14
1·44	0·811	0·7905	5·40 ,,	6·66 ,,	1·90	1·72
0·91	0·564	0·7794	5·52 ,,	9·77 ,,	2·30	2·11
0·75	0·482	0·7761	6·56 ,,	13·59 ,,	3·00	2·76
0·47	0·319	0·7695	5·60 ,,	17·54 ,,	3·13	2·85
0·39	0·268	0·7677	5·21 ,,	19·43 ,,	3·20	2·88
0·33	0·238	0·7656	5·04 ,,	21·65 ,,	3·20	2·90
0·13	0·095	0·7593	4·17 ,,	43·85 ,,	4·30	3·76
0·06	0·044	0·7568	2·42 ,,	55·08 ,,	3·60	2·90
0·115	0·011	0·7542	1·21 ,,	110·8 ,,	3·70	2·15
0·011	0·008	0·7540	1·21 ,,	138·2 ,,	4·08	2·40

independent solutions.   Some measurements with intermediate concentrations are omitted, to save space, but they fit in smoothly with those presented here.

It will be noticed that the conductivity is very low, making accurate measurement difficult. It is, however, sufficiently higher than that of alcohol itself $(4.9 \times 10^{-7}$ at $60°)$ to make it un-mistakable.

In the second place, in contrast to Dennhardt's data (*loc. cit.*), the conductivity rises steadily on dilution. Dennhardt's measurements appear to be inaccurate, and it may be pointed out that Kahlenberg and Schreiner (*Zeitsch. physikal. Chem.*, 1898, **27**, 552) obtained conductivity data for aqueous solutions of sodium oleate which are twice as great as those determined by Dennhardt. In quoting the latter, Goldschmidt remarks (Ubbelohde and Goldschmidt, "Handbuch der Oele und Fette," 1911, III, 47) that the experimental results appear to be due to some error. Again, Dennhardt's data for aqueous potassium oleate differ in some cases from those of Kurzmann (*Koll. Chem. Beihefte*, 1914, **5**, 427) by as much as 30 mhos.

It is very satisfactory to find that the complicated relationships observed by Dennhardt have no real existence, for it would be difficult to explain them, although other similar cases are to be found in the literature of non-aqueous solutions. The point is that they appeared to occur in a substance of simple molecular weight and in regions of extremely low concentration of ions. Thus a mere trace of ion would have to possess a quite impossibly great intrinsic dissociating power, enormously greater even than the sufficiently improbable value ascribed to ionised potassium chloride by Walden (dielectric constant calculated as 14,000). The other alternative would have to be that the ions possessed great tendency towards complex-formation, even in extreme dilution, without, however, an appreciable proportion of the corresponding undissociated complex being formed, even in very concentrated solutions.

Godlewski (*Bull. Acad. Sci. Cracow*, 1904, **6**, 239) found that eight organic acids exhibited in alcohol conductivities of the same order of magnitude as that described above for oleic acid.   Further, these acids obeyed the law of mass action. When the ionisation is so small, the law of mass action requires that $\mu / \sqrt{v}$ should be a constant, where μ is the molecular conductivity and v the dilution in litres.

In table II, the penultimate column contains the values of this expression $\mu / \sqrt{v}$, and the last column the same expression corrected for the conductivity of the alcohol.   In both cases it is quite

definitely shown that the values are not constant for solutions of greater concentration than $N/8$ or $N/2$ respectively, but both expressions are appreciably constant for the more dilute solutions. The uncorrected values must ultimately continue to rise almost in proportion to the dilution, owing to the fact that the specific conductivity is to be very largely ascribed to the alcohol.

The corrected values are constant, for the fifty-fold range of dilution below $N/2$, within the experimental error, which is, however, necessarily rather large. In other words, the law of mass action applies to these results. The conductivity of the highest concentrations diminishes rapidly, obviously because the solvent is being altered from alcohol to a mixture in which oleic acid actually preponderates.

Wightman, Lloyd, Wiesel, and Jones (*J. Amer. Chem. Soc.*, 1914, **86**, 2243; 1916, **88**, 12I') have measured the conductivity of more than forty organic acids in alcohol, including a few of those measured by Godlewski, and find a conductivity of the same magnitude, but the conductivity does not obey the law of mass. Their results, like Wilderman's (*Zeitsch. physikal. Chem.*, 1894, **14**, 231, 247), tend to increase almost as fast as the dilution, instead of being proportional to the square root of the dilution. This deviation from the law of mass action is consequently in the opposite direction from that observed for strong electrolytes in aqueous solution.

It appears possible that Jones's data were not corrected for the conductivity of the alcohol, although in $N/512$-solution this amounted to more than two-thirds of the conductivity. Their results in some cases obey the law of mass action if corrected, some are erratic, a few diminish rapidly, whilst half still rise with dilution.

It is really not surprising that the law of mass action is not always observed, as the relationships are complicated by the esterification which slowly takes place. This must remove hydroxyl ions formed by the alcohol and enhance the amount of ethyl ions present.

The slow esterification does not alter the conductivity much, in spite of the water formed. A $3\cdot4N$(weight)-solution does not alter in conductivity at $60°$ by more than 1 or 2 per cent. in six hours from the time of preparation. According to Jones and his co-workers, a certain amount of esterification must occur, although they found the rate to be independent of the temperature within their experimental error. Dennhardt (*loc. cit.*) found in an $18\cdot4$ per cent. solution of oleic acid in methyl alcohol an increase of only $2\cdot9$ per cent. in fifteen hours at $25°$, and an increase of

.

¼ per cent. in a 36 per cent. solution in fifteen hours. In an 18·5 per cent. solution in ethyl alcohol he observed an increase of 0·2 per cent., and in a 53 per cent. solution an increase of 2·6 per cent. in specific conductivity.

Although in a given time the proportion of acid converted into ester and water would be about the same for any one temperature, independent of the concentration; on diluting there is now more than one substance present, of which the dissociation, and therefore the conductivity, is increasing with dilution. This would seem to explain the general nature of the results, but a study of the esters in alcoholic solution and further knowledge of the part the ions play in the mechanism of the reaction are required for a full discussion of the phenomena.

No stress can be laid on the confirmation of the law of mass action by some acids in alcoholic solution, since all such systems are either in process of reaction or have attained equilibrium through the presence of a large amount of ester.

Mixtures of Oleic Acid and Potassium Oleate in Alcohol.

There is a slight but distinct tendency for oleic acid and potassium oleate to unite, with the formation of a complex. This is shown by the following ebullioscopic data for mixed solutions, where the concentration of the oleate was 0·16N(weight) and that of the oleic acid varied from 0·27N to 0·57N. The molecular weights found were 311·9, 289·1, 296·4, 322·8. Mean, 305·0; Calc.; 282·3. Difference, 7·4 per cent. Found above (p. 440), for pure oleic acid solutions, 287·1.

The conductivity of potassium oleate in alcohol is diminished by the addition of oleic acid to the solution. For instance, 0·28N(weight)-solution of potassium oleate at 60° possessed a specific conductivity of 0·001552; on adding 2·88 equivalents of oleic acid [2·88 × 0·28N(weight)], the specific conductivity was lowered by 44·3 per cent. to 0·000865. A 0·34N(weight)-solution of the oleate exhibiting a conductivity of 0·001381 on addition of 0·164 equivalent (0·164 × 0·34N) of oleic acid gave the value 0·001336, a lowering of 3·3 per cent. Although the lowering is thus proportional to the oleic acid added, the effect is not simply dilution of the solution by indifferent oleic acid, since in the first case the weight of oleic acid was only 21 per cent. of the total weight of solution. This shows again that a certain amount of a complex is formed.

Summary.

In moist as well as in dry alcohol, potassium oleate is a typical simple electrolyte moderately dissociated. Oleic acid, contrary to previous data, is also a normal electrolyte exceedingly little dissociated, but apparently obeying the law of mass action on dilution. In mixtures of oleic acid with potassium oleate, a small amount of a complex compound is formed, which tends to show that a small proportion of the ions of the oleic acid itself are also complex. This trace probably accounts for the slight but distinct tendency of all these solutions towards opalescence and frothing.

XXXVII.—*Synthesis of Pyranol Derivatives.*

By SARAT CHANDRA CHATTERJI and BROJENDRA NATH GHOSH.

IT has been shown by one of us (T., 1915, **107**, 1442) that diketohydrindene condenses with *o*-hydroxyaldehydes, giving ketoindopyranol derivatives of the following type:
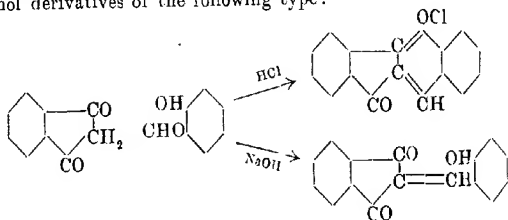
It is apparent that the existence of the $\cdot CO \cdot CH_2 \cdot CO \cdot$ group in diketohydrindene is responsible for these changes, and in order to show that the reaction is a general one, we have extended the investigation to other substances containing this group. In the present paper, we describe experiments with benzoylacetone and acetylacetone. One would expect that in these cases also the

interaction between, say, benzoylacetone and salicylaldehyde would proceed in the normal way, yielding condensation products of the following type:

$$
\begin{array}{ccc}
\text{OH} & \text{COPh} \\
\text{CHO} & \text{CH}_2\text{·COMe}
\end{array}
\rightarrow
\begin{array}{cc}
\text{OH} & \text{COPh} \\
\text{CH=C·COMe}
\end{array}
\rightarrow
$$

$$
\begin{array}{c}
\text{OCl} \\
\text{CPh} \\
\text{C·COMe} \\
\text{CH}
\end{array}
\quad \text{or} \quad
\begin{array}{c}
\text{OCl} \\
\text{CMe} \\
\text{C·COPh} \\
\text{CH}
\end{array}
$$

(I.)   (II.)
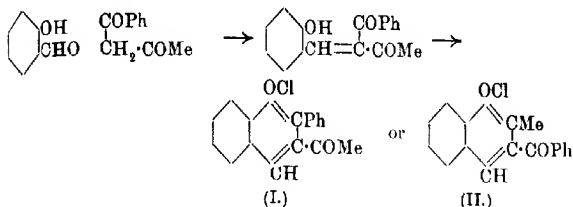
The reaction is not, however, so simple as that indicated by the above equations. Under different conditions, we have been able to isolate three different products from the condensation of these two substances. Two are actually the same as I and II, one being soluble in alcohol and the other insoluble. The former loses hydrogen chloride very readily on exposure to air, and is converted into its base. From its similarity to acetylacetone, we are of opinion that it may have the constitution indicated by I, the insoluble substance having the constitution II. The third product is a complex substance resulting from the reaction of one molecular proportion of salicylaldehyde with two molecular proportions of benzoylacetone, the constitution of which has not yet been determined.

In the case of acetylacetone and salicylaldehyde, two different substances were isolated, one of which was soluble and the other insoluble in acetic acid. In this reaction, the intermediate unsaturated ketone could not be isolated.

In the case of benzoylacetone and salicylaldehyde, the intermediate *salicylidenebenzoylacetone* was obtained by boiling the insoluble compound, formed by their condensation in the presence of hydrogen chloride, with excess of aqueous potassium hydroxide (50 per cent.). The substance, on being boiled with dilute hydrochloric acid, condenses again to the original anhydrohydrochloride (I or II).

The acetyl or benzoyl groups of these substances are very stable, as they are not eliminated on boiling with dilute hydrochloric acid for a long time or even with sodium hydroxide solution.

The bases corresponding with both I and II have also been isolated, their constitutions being represented by the same formulæ except that chlorine is replaced by hydroxyl.

Experimental.

Preparation of Benzoylacetone.

Claisen (*Ber.*, 1887, **20**, 655) prepared this compound by treating a mixture of acetone and ethyl benzoate with alcohol-free sodium ethoxide, but the authors have found the following method much more easy and advantageous.

A mixture of 30 grams of ethyl benzoate and 15 grams of acetone was treated with 50 c.c. of dry ether, and then 4·6 grams of sodium wire or shavings were added. The whole was cooled in water, and the sodium salt at once began to separate. After an hour, the mixture was gently warmed on a water-bath for a few minutes. The precipitate was collected, washed with ether, and then spread on a porous plate. The dried sodium salt was dissolved in a small quantity of hot water, and the cooled solution quickly acidified with dilute sulphuric or acetic acid. The precipitate was collected and washed, and was found to consist of almost pure benzoylacetone.

Condensation of Benzoylacetone and Salicylaldehyde.

Benzoylacetone (6·4 grams) and salicylaldehyde (2·4 grams) were dissolved in the minimum quantity of methyl alcohol, and a current of dry hydrogen chloride was passed through the solution for two hours. The mixture became hot and assumed a dark red colour, but no solid substance separated. After about five hours, the liquid was poured into dilute hydrochloric acid, when a dark green substance separated. This was collected, washed with dilute hydrochloric acid, and finally recrystallised from alcohol containing dilute hydrochloric acid :

0·1389 gave 0·4125 CO_2 and 0·0667 H_2O. $C = 80·9$; $H = 5·3$.

$C_{27}H_{20}O_3,\frac{1}{2}H_2O$ requires $C = 80·8$; $H = 5·3$ per cent.

The compound crystallises in dark green needles which melt at about 120°. It dissolves in acetic acid, yielding a green solution exhibiting a slight green fluorescence. On boiling with hydrochloric acid, the substance remains unchanged. It forms a very unstable hydrochloride which evolves hydrogen chloride on being kept in a desiccator.

3-Acetyl-2-phenyl-1:4-benzopyranol Anhydrohydrochloride (I) or *3-Benzoyl-2-methyl-1:4-benzopyranol Anhydrohydrochloride* (II).

A mixture of 3·2 grams of benzoylacetone and 2·4 grams of salicylaldehyde was dissolved in excess of methyl alcohol, and the

solution cooled in a freezing mixture. A slow current of dry hydrogen chloride was then passed into it, care being taken that no rise of temperature occurred during the reaction. The solution gradually darkened in colour, and a dark red, crystalline substance separated. The mixture was then poured into dilute hydrochloric acid, and the dark, crystalline substance which was obtained in this way was collected and washed with dilute hydrochloric acid. On attempting to recrystallise it from alcohol, it was found that only a small portion of it (B) was soluble in alcohol, whereas the bulk of the precipitate (A) was insoluble in practically all the ordinary solvents. The substance A was kept in a desiccator over potassium hydroxide and analysed:

0·1793 gave 0·4594 CO_2 and 0·0807 H_2O. C = 69·8; H = 5·0.

0·2646 „ 0·1259 AgCl. Cl = 11·8.

$C_{17}H_{13}O_2Cl,\frac{1}{2}H_2O$ requires C = 69·6; H = 4·8; Cl = 12·1 per cent.

It is a black, crystalline substance which does not melt. It dissolves in concentrated sulphuric acid, forming a red solution which does not show any fluorescence.

The *base* corresponding with the salt (A) was prepared by triturating about 1 gram with an excess of a 2 per cent. solution of sodium hydroxide. After keeping the mixture for about half an hour, it was filtered and the residue washed until the filtrate was free from alkali. The substance was then kept in a desiccator over sulphuric acid:

0·1779 gave 0·4679 CO_2 and 0·0916 H_2O. C = 71·7; H = 5·7.

$C_{17}H_{14}O_3,H_2O$ requires C = 71·8; H = 5·6 per cent.

The base is a pale brown substance which is insoluble in all the ordinary solvents. On heating, it does not melt, but chars. It is reconverted into the original salt on being treated with dilute hydrochloric acid.

Salicylidenebenzoylacetone,
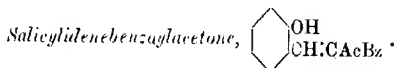
This was prepared by heating the insoluble pyranol anhydrohydrochloride with a 50 per cent. solution of potassium hydroxide for several hours. After being cooled, the mixture was acidified with dilute hydrochloric acid, filtered, and the residue washed with hot water. It is a pale brown substance which does not melt on heating, and changes to a chocolate colour on exposure to air:

0·1865 gave 0·5066 CO_2 and 0·0990 H_2O. C = 74·0; H = 5·8.

$C_{17}H_{14}O_3,\frac{1}{2}H_2O$ requires C = 74·1; H = 5·4 per cent.

Attempts to prepare this substance directly by condensing the

constituents in the presence of piperidine or methyl-alcoholic sodium hydroxide were unsuccessful. In every case, a gummy material separated from which no definite substance could be isolated.

Substance B.—As this was formed in very small amount, we isolated it by condensing molecular quantities of benzoylacetone and salicylaldehyde in excess of methyl alcohol and filtering off the precipitate formed. The alcoholic solution was then mixed with dilute hydrochloric acid, when a brown substance separated, which was collected, washed, redissolved in alcohol, and reprecipitated with dilute hydrochloric acid:

0·1815 gave 0·4757 CO_2 and 0·0813 H_2O.   C=71·4; H=4·9.

$C_{17}H_{13}O_2Cl$ requires C=71·8; H=4·6 per cent.

This pyranol derivative is a pale brown substance which fuses at a high temperature. On keeping it exposed to the moist atmosphere, it slowly hydrolyses, giving off hydrogen chloride, and being converted into the corresponding base.

The *base* was prepared by dissolving the corresponding anhydro-hydrochloride in alcohol and treating the solution with an excess of aqueous sodium acetate. The precipitate was collected, washed with water, and then crystallised from dilute alcohol, when it separated in green prisms, which appeared grey when dry:

0·1426 gave 0·3744 CO_2 and 0·073 H_2O.   C=71·6; H=5·7.

$C_{17}H_{14}O_3,H_2O$ requires C=71·8; H=5·6 per cent.

Condensation of Acetylacetone and Salicylaldehyde.

This condensation product was prepared by dissolving 2 grams of acetylacetone and 2·5 grams of salicylaldehyde in the minimum quantity of methyl alcohol, and then saturating the solution with a rapid stream of dry hydrogen chloride for three hours, care being taken to avoid any rise in temperature. The mixture gradually became dark red and soon deposited crystals. The whole was poured into dilute hydrochloric acid, and the substance was collected, washed, and dried. On boiling with acetic acid, it was found that a large portion of it dissolved, but a small quantity remained insoluble although boiled with much acetic acid. The soluble portion was reprecipitated with dilute hydrochloric acid and kept in a vacuum desiccator:

0·2007 gave 0·5617 CO_2 and 0·1009 H_2O.   C=76·3; H=5·58.

$C_{17}H_{16}O_3$ requires C=76·1; H=5·9 per cent.

It crystallises in violet-coloured prisms, which do not melt but carbonise on heating. It forms a hydrochloride which, on keeping, gradually loses hydrogen chloride and becomes quite free from

the acid after two or three days. It is soluble in pyridine and other solvents of high boiling point.

The *phenylhydrazone* of this substance was prepared by dissolving 1 gram in glacial acetic acid and boiling the solution with an excess of phenylhydrazine for about half an hour. The mixture, after being cooled, was poured into dilute acetic acid, and the precipitate collected, washed, and recrystallised from alcohol, separating in rose-red needles which melt at a high temperature—above 300°:

0·1431 gave 10 c.c. N_2 at 29° and 756 mm. $N = 7·9$.
$C_{23}H_{22}O_2N_2$ requires $N = 7·8$ per cent.

The portion insoluble in acetic acid was kept in a vacuum desiccator over sulphuric acid for several days and then analysed. It was a chocolate-coloured substance which did not melt:

0·1251 gave 0·3383 CO_2 and 0·0605 H_2O. $C = 73·7$; $H = 5·3$.
$C_{24}H_{22}O_5$ requires $C = 73·8$; $H = 5·6$ per cent.

XXXVIII.—*The Abnormality of Strong Electrolytes. Part I. Electrical Conductivity of Aqueous Salt Solutions.*

By JNANENDRA CHANDRA GHOSH.

VAN'T HOFF discovered that aqueous solutions of electrolytes show an abnormal osmotic pressure. For such solutions, as is well known, the equation $PV = iRT$ holds good. Arrhenius suggested that $i = (1-a) + na$, where a is the degree of dissociation and n the number of ions into which a molecule dissociates. According to Arrhenius, there is, therefore, an equilibrium between ions and undissociated molecules in solution. Ostwald attempted to apply the law of mass action to this case of chemical equilibrium, but his dilution law, $\dfrac{a^2}{(1-a)V} = K$ fails absolutely in the case of strong

electrolytes. Various hypotheses have been put forward to explain this anomaly, for example, hydration of ions, change in ionic friction with dilution, formation of complexes, action of salts, change in the dielectric constant of the solvent, interaction between molecules and ions, etc. None, however, has been found to be satisfactory. It appears to the present author that the fundamental suggestion of Arrhenius, postulating the co-existence of undissociated molecules and ions in solution, is probably not valid. The question of chemical equilibrium does not enter into the question at all in the case of strong electrolytes. In solutions of strong electrolytes only ions are present, and the attractive forces between ions are only governed by the physical laws of electrostatic attraction. On the basis of this simple assumption, a quantitative interpretation of the increase of molecular conductivity with dilution will be given.

Number of Free Ions in a Solution containing a Gram-molecule of Salt from the Classical Kinetic Theory.—According to a well-known theorem of the kinetic theory of gases, there is a simple relation between the total number of molecules and the number which can perform the work required to displace a molecule from the sphere of mutual attraction. In applying this theorem to calculate the number of free ions in a solution containing a gram-molecule of salt, we may proceed thus :—A salt solution, where only ions are present, is perfectly analogous to a gaseous system. The electrical attraction between the oppositely charged ions corresponds with the molecular forces in an imperfect gas. Due to this attraction, a field of force exists in the interior of a salt solution, the potential of which may be represented by A, that is, A is the work done when the ions constituting a gram-molecule go beyond one another's sphere of attraction. The ions in a solution are, of course, endowed with a kinetic energy of translation, the distribution of velocities being governed by Maxwell's law. As the work done in escaping from the electrical field inside the solution must be derived from the kinetic energy of the ions, only those ions can escape which have a kinetic energy greater than the work to be done. The problem before us is, therefore, to determine what fraction of the total number of ions has a velocity greater than the critical velocity v_0, where $\frac{1}{2}mv_0^2 = \frac{A}{nN}$. Here N is Avogadro's number $(6 \cdot 16 \times 10^{23}$ Millikan's value), n the number of ions into which a molecule dissociates, and $\frac{A}{nN}$ is therefore the work to be done by each ion before it can escape. Now if V' is the most probable speed of an ion, then the fraction we are considering is

represented by $e^{-v_0^2/V'^2}$ where e is the base of natural logarithm. Now if c is the square root of the mean of the squares of the speeds, we have $c^2 = \frac{3}{2} V'^2$, and the required fraction becomes

$$e^{-\frac{1}{2} v_0^2 / \frac{1}{3} c^2} = e^{-\frac{1}{2} n \cdot N \cdot m v_0^2 / \frac{1}{3} nN \cdot m c^2} = e^{-\frac{A}{nRT}}.$$

(Since there are ions of different equivalent weights in the solution, m signifies the mean mass of an ion.)

As nN is the total number of ions, the number of free ions

$$= nNe^{-\frac{A}{nRT}} \qquad \ldots \ldots \ldots \quad (1)$$

Conductivity of Salt Solutions.—It is well known that Ohm's law holds good for electrolytic conduction. No energy is therefore lost in overcoming the forces of mutual attraction between ions. Any hypothesis put forward to explain the phenomenon of electrolytic conduction must take into consideration this fundamental fact. According to Arrhenius, the molecular conductivity of a salt solution at infinite dilution is at a maximum, because there the salt is entirely dissociated into ions. With diminishing dilution the molecular conductivity diminishes, because the salt is only partly dissociated and hence the number of ions is less. On the hypothesis that in aqueous solutions we have only ions present subject to forces of electrical attraction, a neat explanation can also be given. Since during electrolytic conduction no energy is lost in overcoming the forces of electrical attraction, only those ions take part in the conduction of electricity which by virtue of their kinetic energy can overcome the forces of mutual attraction. These are also the ions which can be liberated on the electrode surface. The rest are inactive so far as electrical conduction is concerned. At any dilution, the number of free conducting ions is equal to

$$n \cdot N \cdot e^{-\frac{A}{nRT}}$$

where A is the work at that dilution. The molecular conductivity is proportional to this number. At infinite dilution A is zero, since the ions are outside one another's sphere of attraction, and therefore the number of conducting ions is nN. Therefore

$$\frac{\mu_v}{\mu_\infty} = \frac{nNe^{-\frac{A}{nRT}}}{nN} = e^{-\frac{A}{nRT}} \qquad \ldots \quad \ldots \quad (2)$$

$$A = nRT \log_e \frac{\mu_\infty}{\mu_v} \qquad \ldots \quad \ldots \quad (2')$$

*The Electrical Work Necessary to Separate the Component Ions
of a Gram-molecule at Various Dilutions.*

(a) *The Arrangement of Ions in Solution.*—In the interior of
a solution, the electrical forces between ions are balanced. In
order that this equilibrium condition may be attained, the ions
should arrange themselves in a definite fashion. It is necessary
that they should adopt a geometrical disposition of perfect regu-
larity, as do the atoms when they assume a crystalline structure,
under the forces of mutual attraction. This does not necessarily
mean that the ions in solution are devoid of any kinetic energy
whatsoever. What we assume here is that the mean disposition of
the oppositely charged ions should conform to some patterns in
space. According to Ostwald, the conditions of the salt molecule
in the crystalline state is not far removed from the state of solu-
tion. Indeed, there is not much difference between a crystalline
salt and the same in a molten condition as regards their electro-
chemical properties. Thus, the experiments of Graetz (*Ann.
Phys. Chem.*, 1890, [iii], **40**, 18) have shown that there is no
sudden change in electrical conductivity as we pass from the solid
to the fused state.

It may well be that even the forces which group the atoms of
a solid salt according to a definite space-lattice are electrical in
nature. In the first place, therefore, we make the perfectly
reasonable assumption that the marshalling of the ions of a salt
in a state of solution is analogous to the arrangement of its atoms
in the crystalline structure.

(b) *The Forces of Electrical Attraction between Ions.*—For the
calculation of the electrical work it is necessary to make another
assumption. In solution, an ion takes up a definite mean position
because of the forces of electrical attraction exerted by oppositely
charged ions surrounding it.

We may, however, suppose that the component ions of a salt-
molecule form a completely saturated electrical doublet. When
a univalent ion tends to pass out of solution, the solution becomes
electrified with an opposite unit charge and attracts it as a whole.
By assuming the existence of electrical doublets we only locate the
centre of attraction inside the solution. The work necessary for
separating the component ions of a molecule is the electrical work
done in moving the ions constituting a doublet from their fixed
mean distance in the solution to an infinite distance apart.
Thus for an aqueous solution of a binary salt like potassium

chloride, the electrical work necessary for separating the potassium and chlorine ions

$$= \frac{E^2}{Dr} \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (3)$$

where E is the charge on each ion, D the dielectric constant of water, and r the distance between the oppositely charged ions at that dilution.

For salts of the type of barium chloride, there are two electrical doublets associated with each molecule, Cl–Ba–Cl. Now let us remove the two chlorine ions successively from the sphere of influence of the barium ion. For the first chlorine ion, the electrical work is $\frac{E^2}{D.r}$, the same as is necessary for separating the components of a doublet in potassium chloride solutions. The removal of the second chlorine ion is much more difficult. This ion is attracted by two opposite charges, and hence the work due to electrical attraction is $\frac{2E^2}{D.r}$. The work necessary for separating the component ions of a molecule of barium chloride is therefore

$$\frac{3E^2}{D.r} \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (4)$$

For salts of the type of magnesium sulphate the electrical work is

$$\frac{4E^2}{D.r} \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (5)$$

for each ion here carries two unit charges. Now, if we can determine the value of r for these types of salt at various dilutions, A is known, and therefore the ratio $\frac{\mu_v}{\mu_x}$, which is equal to $e^{-\frac{A}{nar}}$ can at once be calculated.

(c) *Calculation of the Distance between Ions in Solutions of Binary Salts.*—The distance between the oppositely charged ions in an aqueous solution can be very simply determined on the assumption previously made. Take, for example, the case of potassium chloride. Bragg has actually measured the distance between the planes 100, 110, 111 of this cubic crystal, and has found that it is the simple cubic lattice to which the arrangement of the atoms conforms. We therefore expect that in solutions, also, the sets of points corresponding with the mean position of the ions form a cubic space-lattice. It is obvious that in a cubic lattice there is only one point, that is, one ion, associated with a unit cell, the distance between the oppositely charged ions being

the linear dimension of the unit cell. Since there are $2N$-ions, the total volume occupied by $2N$-unit cubes $= 2N \cdot r^3 = V$ (c.c. containing a gram-molecule), therefore

$$r = \sqrt[3]{\frac{V}{2N}} \text{ and } A = \frac{N \cdot E^2 \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} \quad \cdot \quad \cdot \quad (6)$$

$$= 2RT \log_e \frac{\mu_\infty}{\mu_v} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

where $E = 4 \cdot 7 \times 10^{-10}$ [E.S.U.] and $D = 81$ at $18°$.

For salts like ammonium chloride or potassium nitrate, where complex univalent radicles are encountered, we are also justified in assuming that the distance between ions at equivalent dilutions is approximately the same as in the case of potassium chloride solutions.

(d) *Calculation of the Distance between Ions in Solutions of Salts like Barium Chloride.*—Crystals of calcium fluoride, the constitution of which is perfectly analogous to that of barium chloride, have been thoroughly investigated by Bragg (*Proc. Roy. Soc.,* 1914, A, **89,** 474). In a fluorspar crystal, the calcium atoms are arranged in a face-centred cube lattice, whilst the fluorine atoms occupy the centres of the small cubes. This structure explains how, for each calcium atom, two fluorine atoms may be arranged to form a cubic lattice. Assuming that the arrangement of the barium and chlorine ions in solution corresponds with the fluorspar lattice, we find that each unit cube of the lattice is associated with half an ion of barium. If r be the linear dimension of the unit cube, since there are N-barium ions, $2N \cdot r^3 = V$ (c.c. containing a gram-molecule), therefore

$$r = \sqrt[3]{\frac{V}{2N}}.$$

The chlorine ions, from analogy, should occupy the centres of unit cubes, hence the distance between the barium ion and the chlorine is $\frac{\sqrt{3}}{2} r$. Therefore the electrical work required to separate the components of a gram-molecule is equal to

$$\frac{3NE^2 \cdot 2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt{3} \cdot \sqrt[3]{V}} \text{ ergs}$$

$$= 3RT \log_e \frac{\mu_\infty}{\mu_v} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

(e) *Calculation of the Distance between Ions in Solutions of Salts like Magnesium Sulphate.*—No definite structure has yet been assigned to crystals of magnesium sulphate. The fundamental lattice is, of course, not cubic, but a rhombohedron.

It is possible that, owing to the forces of electrical attraction being greater, the oppositely charged ions constituting a doublet should come together as close as possible. Since, however, we are dealing with a salt, the valency volumes of the ions of which are, according to Barlow and Pope's theory, twice as great as that of a univalent ion, the distance between the doublets should be greater than that in the case of potassium chloride. In solution we may take the cube as the fundamental lattice, without introducing any serious error. The above conditions are satisfied if we imagine that the unit cube is formed only by two oppositely charged ions placed at the adjacent corners. The unit cell becomes thus associated with only one-fourth of an ion, as in the cube-centred lattice. If r be the linear dimension of the unit cube at dilution V, then $8N . r^3 = V$ (c.c. containing a gram-molecule) or

$$r = \sqrt[3]{\frac{V}{8N}} .$$

r is also the distance between the component ions of a doublet. Therefore the electrical work

$$A = \frac{4 . N . E^2 \sqrt[3]{8N}}{D \sqrt[3]{V}} = 2RT \log_e \frac{\mu_\infty}{\mu_v} \quad . \quad . \quad (9)$$

From the equations (7), (8), and (9), which contain no unknown quantities whatever, $\frac{\mu_v}{\mu_\infty}$ can be at once calculated for any dilution. In the following tables it will be shown how the observed values of μ_v at 18° agree with those calculated from the above equations. The value of μ_∞ cannot be determined experimentally, but is generally obtained by extrapolation. In the tables, the value of μ_∞ has been calculated from the observed values of μ_v for $0.01N$-solutions, and this theoretical value of μ_∞ has then been utilised in calculating μ_v at other dilutions. The observed values of $\mu_v . \times \mu_v$ are from the tables of Kohlrausch and co-workers.

TABLE I.

$V = Dilution\ in\ litres.$

Salt.	μ_∞ calc. from μ_{100}		$v = 10.$	20.	100.	1000.	5000.
KCl	132·2	μ_v calc.	111·7	115·7	122·5	127·7	129·2
		μ_v obs.	112·0	115·9	122·5	127·6	129·1
NaCl	110·3	μ_v calc.	93·1	96·5	102·0	106·4	108·0
		μ_v obs.	92·0	95·7	102·0	106·5	107·8
LiCl	99·6	μ_v calc.	84·0	87·1	92·1	96·2	97·5
		μ_v obs.	82·4	86·1	92·1	96·5	97·8
CsCl	135·4	μ_v calc.	114·3	—	125·2	130·6	132·5
		μ_v obs.	113·6	—	125·2	130·6	132·0

TABLE I.—(continued).

$V = Dilution$ in litres.

Salt.	μ_∞ calc. from μ_{100}		$v = 10.$	20.	100.	1000.	5000.
NH$_4$Cl ...	132·0	μ_v calc.	111·3	115·4	122·1	127·4	129·3
		μ_v obs.	110·7	115·2	122·1	127·3	128·8
KBr	134·5	μ_v calc.	113·6	117·7	124·4	129·7	131·7
		μ_v obs.	114·2	117·8	124·4	129·4	130·9
KI	133·5	μ_v calc.	112·7	116·7	123·4	128·7	130·6
		μ_v obs.	113·9	117·2	123·4	128·2	129·5
KNO$_3$ ...	127·9	μ_v calc.	107·8	111·2	118·1	123·3	124·8
		μ_v obs.	105·0	110·0	118·1	122·9	124·3
NaNO$_3$ ...	105·0	μ_v calc.	88·5	91·8	97·1	101·3	102·8
		μ_v obs.	87·4	91·4	97·1	101·8	103·3
C$_2$H$_3$O$_2$K	101·6	μ_v calc.	85·9	88·9	94·0	98·1	99·6
		μ_v obs.	84·0	87·7	94·0	98·3	99·6

The agreement is remarkably good. The difference between the observed and the calculated values is rarely greater than 1 per cent.

TABLE II.

$V = Equivalent$ dilution in litres.

μ_v and μ_∞ are equivalent conductivities.

Salt.	μ_∞ calc. from μ_{100}		$v = 10.$	20.	100.	1000.	5000.
BaCl$_2$	124·3	μ_v calc.	92·0	97·3	107·7	116·2	119·5
		μ_v obs.	92·2	96·8	107·7	116·9	119·8
SrCl$_2$	121·6	μ_v calc.	89·3	95·2	105·4	113·8	116·9
		μ_v obs.	90·2	94·4	105·4	114·5	117·5
CaCl$_2$	119·1	μ_v calc.	87·5	93·2	103·2	111·4	114·6
		μ_v obs.	87·9	92·8	103·2	111·5	114·4

The difference between the theoretical and the observed values is never greater than 1 per cent.

TABLE III.

$V = Equivalent$ dilution in litres.

μ_v is equivalent conductivity.

Salt.	μ_∞ calc. from μ_{100}		$v = 10.$	20.	100.	1000.
MgSO$_4$	114·7	μ_v calc.	48·1	57·6	76·6	95·1
		μ_v obs.	50·1	57·0	76·6	100·2
ZnSO$_4$	110·0	μ_v calc.	46·0	55·1	73·4	91·0
		μ_v obs.	46·2	53·5	73·4	98·0
CuSO$_4$	108·0	μ_v calc.	45·2	53·0	72·2	89·6
		μ_v obs.	45·0	51·4	72·2	101·6

At $V=100$ the discrepancy is very large. Below $V=100$ the agreement is quite good. At high dilutions the conductivity is much greater than the calculated value, because of the undoubted hydrolysis of the salts—the interaction between ions and water molecules.

The Temperature-coefficient of the Ratio $\frac{\mu_v}{\mu_\infty}$.—We have seen how the observed values of μ_v agree with those calculated from the equations (7), (8), and (9). There is every reason to believe that the laws of electrical attraction are independent of temperature. The equations, which yield very satisfactory results at 18°, should also hold good at higher temperatures. In our equation for binary electrolytes,

$$A = \frac{N \cdot E^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} = 2RT \log_e \frac{\mu_\infty}{\mu_v}$$

if the variation of the dielectric constant of water with temperature be known, $\frac{\mu_v}{\mu_\infty}$, can be easily calculated for any temperature. According to Drude, the variation of the dielectric constant of water with temperature between 0° and 76° is given by the following formula:

$$D_t = D_{18}\{1 - 0.00436(t-18) + 0.0000117(t-18)^2\}.$$

Assuming that this formula holds good up to 100°, the dielectric constant of water at $100^\circ = 52.6$. Table IV shows how the calculated values of $\frac{\mu_m}{\mu_\infty}$ at various temperatures agree with the observed data of Noyes and Coolidge (*Zeitsch. physikal. Chem.*, 1903, **46**, 323).

TABLE IV.

Salt.	T°.		$v = 12.5$.	$= 100$.
KCl,	18°	$\frac{\mu_v}{\mu_\infty}$ calc.	85·4 per cent.	93·0 per cent.
		$\frac{\mu_v}{\mu_\infty}$ obs.	87·0 ,,	94·0 ,,
	100°	$\frac{\mu_v}{\mu_\infty}$ calc.	82·6 ,,	90·9 ,,
		$\frac{\mpi_v}{\mu_\infty}$ obs.	82·6 ,,	91·1 ,,

The coincidence is remarkable. The diminution of the ratio $\frac{\mu_v}{\mu_\infty}$ with increase in temperature may thus be quantitatively explained.

In conclusion, reference should be made to one important point, namely, the question of weak electrolytes. They are invariably either acids or bases. The abnormally high conductivity of hydrogen and hydroxyl ions leaves no room for doubt that here there is a chemical interaction between solvent and solute molecules. Ostwald's dissociation constant is probably related in some way to the constant of these specific chemical reactions.

I take this opportunity of offering my best thanks to Mr. J. N. Mukherjee, M.Sc., for many valuable suggestions. My best thanks are also due to Prof. P. C. Râp.

XXXIX.—*Spinacene and some of its Derivatives.*

By A. CHASTON CHAPMAN.

IN a recent communication (T., 1917, **111**, 56) describing the preparation and properties of spinacene and of some of its derivatives, I directed attention to the fact that the formula for the hydrocarbon based on the analysis of the hexahydrochloride (which was the most crystalline and best defined compound I had succeeded in obtaining) was not in good agreement with the results for the determination of the molecular weight by the cryoscopic method. This discrepancy I was unable to explain, and I therefore determined to prepare a further and larger quantity of the hydrocarbon and also of the hydrochloride. I was fortunately able to obtain some more of the shark-liver oil, and proceeded to prepare spinacene from it by the method previously adopted. As in my earlier work, the main fraction boiled within a range of a few degrees and contained only about 0·5 per cent. of oxygen.

As I had reason to believe that metallic sodium was without action on the hydrocarbon, I proceeded to distil it with the addition of some sodium for the purpose of obtaining a product free from oxygen. In my earlier work, only about 50 c.c. of the oil had been distilled in this manner, and then under a pressure of 10 mm. In the present case, a much larger volume of the oil was employed, and owing to the faulty working of the pump, the pressure during distillation remained constant at about 45 mm.,

the bulk of the oil distilling under that pressure at about 290°. It was noticed that during the distillation the liquid in the flask became increasingly dark in colour, and towards the end had become converted into an almost black, tarry mass.

The portion of the oil, which had distilled over between 280° and 295°, was then submitted to fractional distillation (without sodium) at a pressure varying from 35 to 40 mm., and it was found that the boiling point rose gradually from 84° to 298°.

From this result, it is evident that in the presence of sodium and under the conditions above mentioned, spinacene undergoes some decomposition, and that this method cannot consequently be adopted for its purification. I therefore decided to prepare some more of the spinacene by fractional distillation without the use of sodium and at a pressure not exceeding 10 mm. In these circumstances, a large specimen of the hydrocarbon was obtained having the following properties:

Boiling point	260° (corr.)/9 mm.
Specific gravity (15°/15°)	0·8610
Refractive index at 20°..............	1·4956

When examined by the Wijs method, it was found that 100 parts of the hydrocarbon united with 367·9 parts of iodine.

The following molecular weight determinations were made by the cryoscopic method:

   I. 0·2262 in 16·83 benzene gave $\Delta^t = -0·167°$. M.W. = 394.
   II. 0·2371 in 17·07 benzene gave $\Delta^t = -0·174°$. M.W. = 391.

This number is higher than that given in my previous aper, and in view of the results obtained in the distillation of is larger quantity of hydrocarbon, the discrepancy is readily xplained. Although the breaking up of spinacene when distilled ver sodium does not appear to take place at all rapidly until a mperature corresponding with a pressure of about 40 to 50 mm. reached, there can be no doubt that a little decomposition does xur even at lower temperatures, and that the hydrocarbon which originally used for the molecular weight determinations must ave been contaminated with a little of the decomposition products lower boiling point.

It may be recalled that the average results of five analyses of · e hydrocarbon given in my previous paper were as follows:

$$C = 87·75 ; \quad H = 12·45.$$

The above results therefore agree well with the formula $C_{29}H_{48}$, hich requires $C = 87·88$; $H = 12·12$ per cent. M.W. = 396.

Taking the previously determined number for the specific refrac- on, namely, 0·3394, the molecular refraction is 134·4. Employ-

                                       T

ing Conrady's average numbers for the atomic specific refractions (*D*-line), $C_{29}H_{48}$ with six ethenoid linkings requires 134·3. Taking the specific dispersive power of spinacene as 0·0114, its molecular dispersion, $(r\gamma - r\alpha)M$, is 4·51. Taking Eisenlohr's numbers for the atomic dispersion for the *a*- and the γ-hydrogen lines, the calculated number is 4·21.

As the results of the analysis of the hexahydrochloride which I had previously prepared were in fair agreement with the higher formula, $C_{30}H_{50}$, I determined to prepare a larger quantity of this compound and to submit it to a very thorough process of purification. It was prepared as before, by passing dry hydrogen chloride into a well-cooled solution of spinacene in dry ether. The resulting hexahydrochloride was then purified by dissolving it in warm benzene and adding alcohol until the compound commenced to separate, and finally by crystallising from warm benzene alone. Chlorine estimations were made in each crop of crystals, and the process of recrystallisation was repeated until the chlorine percentage, which showed a tendency to increase, became constant. After the third recrystallisation, the substance was analysed, with the following results:

0·2020 gave 0·2814 AgCl.   Cl = 34·45.
0·2145   „   0·2990 AgCl.   Cl = 34·49.
$C_{29}H_{48},6HCl$ requires Cl = 34·60 per cent.

In the process of recrystallisation, the melting point also rose, the final preparation becoming pasty at about 120° and melting to a clear liquid at 126°. During this process of recrystallisation, a small quantity of an oily substance containing about 24 per cent. of chlorine was separated from the mother liquors. It will be seen that the above result is in far better agreement with the formula $C_{29}H_{48}$ than with the formula previously suggested, namely, $C_{30}H_{50}$, which requires Cl = 33·86 per cent. A 5 per cent. solution of the hydrochloride in benzene was found to be optically inactive.

When heated for some time with boiling water, in which it appears to be quite insoluble, no decomposition occurred. When heated, however, for some time with a mixture of alcohol and water, the crystals soon became pasty, and the liquid, after filtering, gave a strong reaction for chloride.

In the course of these experiments, a further quantity of the oily hydrochloride soluble in ether was obtained, but there is some doubt as to the definite character of this compound, and a further study renders it very doubtful whether it constitutes a product intermediate between the hydrocarbon and the crystalline hexahydrochloride.

Decomposition of Spinacene Hexahydrochloride by Heat.

I have previously directed attention to the fact that, when this compound is heated to a temperature above its melting point, hydrogen chloride is liberated. 2·14 Grams of the hydrochloride were introduced into a weighed test-tube, which was connected with a vacuum pump. The tube was then immersed in an oil-bath and heated for four hours to 150°. Hydrogen chloride was freely evolved, particularly at the commencement of the experiment, and at the end of the above time it was found that 0·32 gram of hydrogen chloride had been lost. The heating was then continued, but as the evolution of gas became very slow, the temperature of the bath was raised to 190°, at which temperature it was maintained for seven hours. At the end of this time, a further 0·36 gram of hydrogen chloride had been given off, making a total loss of 0·68 gram, the total amount present in the hydrochloride taken being 0·76 gram. At this point, the evolution of hydrogen chloride had become so slow that the experiment was stopped.

The oil remaining in the tube was fairly mobile and of a pale· red colour. The iodine value of this oil was 255·5, and it contained Cl = 5·2 per cent. A 10 per cent. solution in benzene was found to be optically inactive.

From this experiment, it would appear that the hydrocarbon left after expelling the hydrogen chloride by heat differs from the original spinacene in being less unsaturated, due probably to the occurrence of some intramolecular change, such as that involved in the conversion of pinene into camphene. The molecular weight of this oil determined by the depression of the freezing point in benzene solution was 479, showing that, in addition to the above intramolecular change, there had been some polymerisation.

Action of Hydrogen Bromide. Spinacene Hexahydrobromide.

Dry hydrogen bromide was passed into a well-cooled solution of spinacene in several times its volume of dry ether. Shortly after the liquid had become saturated, a white substance formed, which appeared to consist of a crystalline substance and an oil. A further quantity of dry ether was added, and the precipitate was separated, washed with ether, and dried. This substance was purified by dissolving it in benzene, adding alcohol until the separation of the compound just commenced, and finally by recrystallisation from benzene alone. After three recrystallisations, the product appeared to be pure, and gave on analysis the following results:

0·2061 gave 0·2640 AgBr.   Br = 54·51.

   $C_{29}H_{48},6HBr$ requires Br = 54·42 per cent.

As in the case of the hydrochloride, it will be seen that this percentage accords much better with the formula $C_{29}H_{48}$ than with $C_{30}H_{50}$, the theoretical percentage of bromine in the latter case being 53·57.

The hexahydrobromide is a brilliant, white, crystalline compound closely resembling the hydrochloride in appearance as well as in respect of its solubility in the commoner solvents. As in the case of the hexahydrochloride, the yield is not very large, oily compounds being formed at the same time. Thus, in one experiment in which a solution of 5 grams of spinacene in 10 c.c. of ether was saturated with hydrogen bromide and allowed to remain for twenty-four hours, the yield of the hydrobromide did not exceed 6·5 grams. When heated, the crystals soften at about 126° and melt to a clear liquid at about 132°. When heated to a still higher temperature, decomposition occurs, hydrogen bromide being freely evolved.

I have devoted a good deal of care to the purification of the hydrochloride and hydrobromide of spinacene, since these compounds are definite and well crystalline, and consequently afford the best indication as to the correct molecular formula of the hydrocarbon. It will be seen that all the results given above agree well with the formula $C_{29}H_{48}$, and although the other derivatives described in my previous communication are less well defined than the hydrogen haloids and not very easily purified, attention may be directed to the fact that, with one exception, the analytical results in all cases agree better with the formula $C_{29}H_{48}$ than with $C_{30}H_{50}$. This will be more clearly seen by reference to the following numbers:

	Found.	$C_{29}H_{48}$.	$C_{30}H_{50}$.
Spinacene trinitrosochloride:			
Cl =	18·48	18·00	17·50
N =	7·36	7·10	6·92
Spinacene trinitrolpiperidide:			
N =	11·52	11·38	11·20
Spinacene trinitrolbenzylamide:			
N =	10·58	10·45	10·27
Spinacene hexanitrosochloride:			
N =	10·62	10·65	10·46
Cl =	27·42	27·00	26·52
Spinacene nitrosate:			
N =	12·80	12·50	12·30

The single exception referred to above is the dodecabromide, which contains Br = 69·7 as compared with 70·79 per cent. required for the lower molecular formula and 70·07 per cent. for the higher. I have already indicated, however, that the action of bromine on

spinacene is very complicated, both addition and substitution derivatives being simultaneously formed. The bromine compound is, moreover, either insoluble or only very sparingly soluble in the great majority of the ordinary organic solvents, and could only be purified by the addition of alcohol to its solution in tetrachloroethane. It is quite possible, therefore, that this compound has not as yet been obtained in a state of purity.

Action of Nitric Acid on Spinacene.

Nitric acid (D 1·42°) mixed with an equal volume of water was added to spinacene and the mixture warmed. A very vigorous reaction occurred with the evolution of oxides of nitrogen. After the reaction had subsided, water was added, and the solid substance which was formed was collected, washed, and dried. It was purified by dissolving it in aqueous sodium hydroxide and by completely saturating the solution with carbon dioxide. The precipitate which formed was separated by filtration, and the clear filtrate, on acidification with dilute sulphuric acid, gave a further precipitate. The latter substance was almost insoluble in ether or petroleum, but moderately soluble in alcohol. It dissolved readily in glacial acetic acid, from which solvent it was obtained by the gradual addition of water as a pale yellow precipitate.

It is clear that in the above experiment at least two products are formed, and doubtless others could be obtained by modifying the conditions of nitration.

Decomposition of Spinacene by Heat in the Presence of Sodium.

At the commencement of this paper, I referred to the fact that a considerable quantity (about 500 c.c.) of spinacene had been distilled over sodium at temperatures corresponding with a pressure of about 45 mm., and that evidence was obtained that under these conditions some decomposition had occurred. The oil which distilled over between 280° and 295°, and measured about 400 c.c., was submitted to fractional distillation (without sodium) under a pressure of about 40 mm. The following four fractions were finally obtained :

(1) 84—88° (about 60 c.c.).
(2) 155—175° (about 60 c.c.).
(3) 220—275° (about 80 c.c.).
(4) 295—298° (about 150 c.c.).

An almost colourless, viscous substance remained in the flask.

The first of the above fractions, which consisted of a fragrant,

mobile liquid, was purified by steam distillation, followed by fractional distillation. The greater portion (about 50 c.c.) boiled constantly at 69°/20 mm.:

0·1097 gave 0·3470 CO_2 and 0·1286 H_2O. C = 86·26; H = 13·02.
0·1121 „ 0·3555 CO_2 „ 0·1301 H_2O. C = 86·48; H = 12·89.

From the above, it was clear that this liquid consisted of a hydrocarbon and contained about 0·6 per cent. of oxygen. It was therefore redistilled several times over sodium, and the portion boiling at 51—54°/10 mm. again submitted to analysis:

0·1291 gave 0·4120 CO_2 and 0·150 H_2O. C = 87·02; H = 12·90.
$C_{10}H_{18}$ requires C = 87·0; H = 13·0 per cent.

This hydrocarbon boils under the ordinary pressure at 170—175°, a little polymerisation apparently occurring during the process. It is optically inactive. The following molecular weight determination was made by the cryoscopic method:

0·4021 in 16·36 benzene gave $\Delta^t = -0·909°$. M.W. = 135.
$C_{10}H_{18}$ requires M.W. = 138.

Its specific gravity at 15°/15° = 0·8149 and at 20°/20° = 0·8125. Its index of refraction at 15° = 1·4588 and at 20° = 1·4565.

Its specific refraction calculated by the $\dfrac{n^2-1}{(n^2+2)d}$ formula is 0·3353 and the molecular refraction is 46·3.

Taking Conrady's average numbers for the atomic specific refractions (D-line), $C_{10}H_{18}$ with one ethenoid linking requires 45·8.

The following estimations were made of the amount of bromine capable of uniting with the hydrocarbon. The bromine was dissolved in carbon tetrachloride and added to a carbon tetrachloride solution of the hydrocarbon under water, the liquid being cooled by means of ice. By working in this way, a correction could be made for the small amount of hydrogen bromide formed as the result of simultaneous substitution. The following are the results of two experiments:

	A.	B.
Substance taken	0·1878 gram	0·1348 gram
Bromine uniting with hydrocarbon...	0·2264 „	0·1646 „

Both these numbers are in close agreement with the addition of two atoms of bromine to one molecule of the hydrocarbon.

All these results point to this substance being a cyclodihydroterpene, and its properties appear to suggest that it may prove to be identical with cyclodihydromyrcene or with cyclolinaloolene. It may be of interest to give for purposes of comparison the physical

properties of *cyclo*dihydromyrcene (*Ber.*, 1901, **34**, 3128) and of *cyclo*linaloolene (*Ber.*, 1894, **27**, 2521):

	Hydrocarbon from spinacene.	*cyclo*Dihydro-myrcene.	*cyclo*Lina-loolene.
Molecular formula	$C_{10}H_{18}$	$C_{10}H_{18}$	$C_{10}H_{18}$
Boiling point	170--175°	169—172°	165—167°
Specific gravity	0·815	0·828	0·811
Refractive index..................	1·459	1·462	1·460
Number of atoms of bromine added ....:..............	Two	Two	Two

Had time permitted, specimens of *cyclo*dihydromyrcene and of *cyclo*linaloolene would have been prepared for the purpose of making a fuller comparison. This I hope will be done at some future time. In the above work, steps were taken to make it quite clear that this terpenic hydrocarbon was not formed by the action of sodium on the small amount of oxygenated constituent occurring in the spinacene used. To this end, the spinacene, after having been distilled over a considerable excess of sodium under 10 mm. pressure, was then redistilled over a further quantity of sodium under 40 mm. pressure. From the distillate, the terpenic hydrocarbon described above was separated by steam distillation. The recovered and unchanged spinacene was then for a third time distilled over sodium under 40 mm. pressure, with the result that a further quantity of the terpenic hydrocarbon was obtained. There can, therefore be no reasonable doubt that this *cyclo*dihydroterpene does, in fact, result from the breaking up of the spinacene molecule. The view which I ventured to put forward in my first communication, that spinacene would prove to be related in some way to the terpenes, is therefore correct. The presence in large quantities in fish-liver oil of a complex hydrocarbon closely related to the terpenes is, I think, of very considerable interest both from the chemical and from the physiological points of view. In this connexion, it may be recalled that there is very strong evidence that cholesterol, a substance having nearly the same number of carbon atoms in its molecule as spinacene and occurring also in fish-liver oils, is a complex terpene compound.

The second fraction obtained from the decomposition of spinacene was also a fragrant, tolerably mobile liquid, boiling at 109—115°/ 10 mm., having an average molecular weight of about 190 and a specific gravity at 15°/15°=0·868 and at 20°/20°=0·865. This, as well as the viscous products left in the distillation flask, which doubtless consist of polymerisation products formed during the process, will, it is hoped, be subjected later on to a further study. Except perhaps in one direction in which results of industrial

importance may be anticipated, the further examination of spinacene and its derivatives will have to remain in abeyance until more normal conditions again prevail.

8 DUKE STREET,
    ALDGATE, E.C.3.   [*Received, May 2nd,* 1918.]

Organic Chemistry.

Preparation of Paraffins. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 296741; from *Chem. Zentr.*, 1917, i, 611).— Alcohols are converted into their formates, and these are heated. Thus, *dihydrocholesteryl formate,* narrow tablets, m. p. 84°, when heated at 290°/10 mm., yields cholestane, and myricyl alcohol gives triacontane. The products are purified by mixing the ethereal solutions with acetic anhydride and concentrated sulphuric acid, and evaporating the ether, when the pure hydrocarbons separate.

J. C. W.

Some Reactions of Acetylene. W. R. HODGKINSON (*J. Soc. Chem. Ind.*, 1918, **37**, 86—87T).—Iron, nickel, cobalt, and to a less extent manganese, tungsten, platinum, and palladium, react with acetylene when heated in this gas or in a mixture of the same with an inert gas. More or less carburisation of the metal results, and at the same time some of the metal enters into the soot-like deposit around the metal. This volatilisation of the metal is practically complete in the case of nickel when the heating is prolonged for a few hours; the soot contains up to 15% of nickel, whilst in experiments with iron it contains 3% of the metal. The carburisation of iron by acetylene is very rapid above 800°, and iron, nickel, and cobalt are still more rapidly carburised by a mixture of ammonia and acetylene. Iron is converted into its nitride by heating it at 800° in ammonia; the nitride when heated in acetylene loses its nitrogen, and the iron becomes highly carburised. Cadmium, zinc, lead, tin, copper, and aluminium do not react with acetylene when heated in this gas. Benzene, toluene, phenol, aniline, naphthalene, etc., behave in a similar manner to acetylene when their vapours are passed over heated nickel or iron.

W. P. S.

The Chemical Actions of the Penetrating Radium Radiation. X. The Influence of the Penetrating Rays on Chloroform and Carbon Tetrachloride. The Action of Ultraviolet Light on Chloroform. ANTON KAILAN (*Monatsh.*, 1917, **38**, 537—552. Compare Hardy and Willcock, A., 1903, ii, 622; Jorissen and Ringer, A., 1907, ii, 520).—The effect of the silent electric discharge alone (Losanitsch, A., 1910, i, 1) and in the presence of hydrogen (Besson and Fournier, A., 1910, i, 349) on chloroform has already been examined. It is now shown that the chief product of the action of the penetrating radium rays for three years on chloroform is hexachloroethane, formed probably by oxidation of the chloroform; chlorine is also produced, but almost completely disappears again by converting the chloroform into carbon tetrachloride and hydrogen chloride. During the exposure, the

chloroform became slightly turbid, and showed an alteration from $D_4^{23\cdot1}$ 1·4731 to 1·4755. With carbon tetrachloride, the density increased from D_4^{25} 1·5843 to 1·5845, and the main chemical alteration was the formation of chlorine and hydrogen chloride, the latter being produced by the action of moisture on transiently existent carbonyl chloride, which together with chlorine is produced by the action of oxygen on the carbon tetrachloride; a small quantity of hexachloroethane was also obtained, doubtless by the reaction $2CCl_4 = C_2Cl_6 + Cl_2$. A mixture of β- and γ-rays, and also γ-rays alone, produce a slight effect on chloroform, an increase in density being perceptible. The three years' exposure to the penetrating rays indicated a comparable degree of susceptibility of chloroform and carbon tetrachloride, but the total amount of decomposition in each case was less than 1%. Ultra-violet radiation exerted a similar but more rapid effect than radium radiation on chloroform: the chloroform became turbid and changed from D_4^{25} 1·4744 to 1·4762 in one day; hydrogen chloride, hexachloroethane, and an amorphous, reddish-brown solid were detected in the liquid.

D. F. T.

Liberation of Hydrogen Chloride from Trichloroethylene.

W. ELSNER (*Chem. Zeit.*, 1917, **41**, 901—902).—In the recovery of trichloroethylene, which had been used to dissolve resin, it was found that a considerable quantity of hydrogen chloride was formed by the decomposition of the solvent. This decomposition was not brought about by the presence of metals, since the distillation was carried out in glass apparatus, and it was evidently due to the action of resin acids and a small quantity of water. The quantity of hydrogen chloride formed amounted to about 5% of the weight of the solvent.

W. P. S.

History of Alcohol.

EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1917, **41**, 865, 883—885, 909—911).—A description of the earlier writings on the preparation of alcohol with some sixty-seven references to literature.

W. P. S.

Alcohol and Soda Lime.

BURT H. CARROLL (*J. Physical Chem.*, 1918, **22**, 128—149).—When the vapour of ethyl alcohol is passed over soda lime heated at temperatures between 250° and 450°, reaction takes place in accordance with the equation $C_2H_5 \cdot OH + NaOH = CH_3 \cdot CO_2Na + 2H_2$. The secondary reaction, $CH_3 \cdot CO_2Na + NaOH = Na_2CO_3 + CH_4$, begins at about the same temperature, and increases so rapidly with the temperature that at 450° the acetate is decomposed almost as quickly as it is formed. It is found that the sodium hydroxide is the active constituent of the soda lime. At the temperatures used, lime was found to have but little effect on the alcohol, whereas sodium hydroxide reacts more quickly than soda lime. The advantage of using soda lime in preference to sodium hydroxide for the experiments is to be found in the fact that the hydroxide is liquid at the temperatures employed.

It is probable that the conversion of alcohol into acetate involves

three stages, in the first of which acetaldehyde is formed, the sodium hydroxide acting as catalyst. Acetaldehyde is, in fact, found amongst the products when sodium hydroxide is used. Special experiments made with acetaldehyde have shown that this is rapidly decomposed in presence of sodium hydroxide, and it is supposed that the acetaldehyde formed in the first stage is then decomposed according to the equation $CH_3 \cdot COH = CH_2 \colon CO + H_2$, with the formation of keten. The keten then reacts with the sodium hydroxide to form sodium acetate, $CH_2 \colon CO + NaOH = CH_3 \cdot CO_2Na$. The formation of keten has not actually been shown, but this is considered to be the probable course of the reaction.　　H. M. D.

Preparation of Acetic Acid from Acetaldehyde. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P., 296282, addition to 294724; from *Chem. Zentr.*, 1917, i, 461. Compare A., 1917, i, 377).—Instead of iron compounds, such substances as nickel acetate or animal charcoal may be used as catalysts.　　J. C. W.

The Scale of Influence of Substituents in Paraffin Mono-basic Acids and the Correlation of Ionisation with Structure. III. The Bivalent Oxygen Atom in the ε-Position. C. G. DERICK and R. W. HESS (*J. Amer. Chem. Soc.*, 1918, **40**, 537—558).—After replying to the criticism by Wegscheider (A., 1912, ii, 529) of the "place factor" and "rule of thirds" mentioned in earlier papers (Derick, A., 1911, ii, 712; 1912, i, 188), and giving recalculated ionisation constants for various organic acids based on modern conductance units, an investigation of the ionisation constant of ε-keto-n-heptoic acid is described. From the determined value $1 \cdot 926 \times 10^{-5}$ for the ionisation constant of this acid and a value $1 \cdot 4 \times 10^{-5}$ chosen from earlier results as approximating to the ionisation constant of n-heptoic acid (Franke, A., 1895. ii, 252; Drucker, A., 1905, ii, 680), the "relative place influence" of the ε-ketonic oxygen atom, indicating its influence relative to that of the two corresponding hydrogen atoms in n-heptoic acid, is calculated to be $0 \cdot 14$.

The requisite ε-keto-n-heptoic acid was prepared by starting from trimethylene glycol, converting this by the action of excess of hydrobromic acid into trimethylene bromide, which on reaction in methyl alcohol with a semi-molecular proportion of potassium cyanide yielded γ-bromobutyronitrile. This product was caused to undergo condensation with ethyl sodioacetoacetate, with formation of *ethyl δ-cyano-α-acetovalerate*, $CN \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHAc \cdot CO_2Et$, a colourless, viscous liquid, b. p. 154°/2 mm., accompanied by some *ethyl αη-dicyano-δ-acetyl-n-heptane-δ-carboxylate*,

$$CO_2Et \cdot CAc(CH_2 \cdot CH_2 \cdot CH_2 \cdot CN)_2,$$
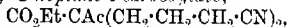
a colourless solid of nutty odour, m. p. 76·5°, b. p. approx. 200°/ 5 mm. The former on hydrolysis with hydrochloric acid gave ethyl alcohol, carbon dioxide, ammonia, and ε-keto-n-heptoic acid, $CH_3Ac \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, b. p. 181—182°/25 mm., 160°/ 13 mm., m. p. 36·5° (compare Perkin, T., 1890, **57**, 230; Blaise and Köhler, A., 1909, i, 204).　　D. F. T.

Production of Organic Compounds containing Phosphorus. J. D. RIEDEL (D.R.-P., 299992; from *Chem. Zentr.*, 1917, ii, 510).—Unsaturated hydroxy-fatty acids of high molecular weight on treatment with phosphorus trihaloids or oxyhaloids yield as primary products acid haloids in which the hydroxyl group is intact; on hydrolysis of these products with water, phosphorus derivatives of the hydroxy-acids are obtained which may be converted into the salts of the alkaline earth metals in the usual way. Ricinstearolic acid and ricinolic acid on treatment with phosphorus trichloride or tribromide yield *compounds* $C_{18}H_{33}O_5P$ and $C_{18}H_{35}O_5P$ respectively.   D. F. T.

The Formation and Decomposition of some Organic Halogenated Compounds. II. EINAR BIILMAN (*Rec. trav. chim.*, 1918, **37**, 245—250. Compare A., 1917, i, 378).—The action of potassium iodide on dibromosuccinic acid in the presence of sulphuric acid is shown to be bimolecular, the product being fumaric acid. The reaction with *iso*dibromosuccinic acid could not be followed quantitatively, owing to the rapidity with which this acid decomposes, giving hydrogen bromide. With benzylbromomalonic acid the action is $CH_2Ph \cdot CBr(CO_2H)_2 + 3KI + H_2O = CH_2Ph \cdot CH(CO_2H)_2 + KI_3 + KBr + KOH$, but a velocity constant for the reaction could not be determined, since the iodine acted on the benzylmalonic acid formed.   W. G.

The Nature of the Inositol Phosphoric Acids of some important Feeding Materials. J. B. RATHER (*J. Amer. Chem. Soc.*, 1918, **40**, 523—536. Compare A., 1917, i, 315).—By hydrolysis of wheat bran with dilute hydrochloric acid, it is possible to obtain an acid, $C_{12}H_{41}O_{42}P_9$ or $C_6H_6(OH)(H_2PO_4)_5$, m. p. 215—216°, which can be separated from accompanying products by means of its strychnine salt, m. p. 220—222°; the latter of the two possible formulæ is preferred, and the compound is described as inositol pentaphosphoric acid; the *silver* salt is amorphous. The method described by Anderson as yielding an inositol hexaphosphoric acid (*N.Y. Geneva Expt. Sta. Tech. Bull.*, 40) is shown to give the pentaphosphoric acid as the main product. Experiments with maize, rice bran, oats, kafir corn, wheat shorts, and rice polish, show the principal inositol phosphoric acid to correspond with the above composition. It is possible that other inositol phosphoric acids may be formed from these materials, but the inositol pentaphosphoric acid, together with orthophosphoric acid, constitute on the average 95% of the acid-soluble phosphorus.   D. F. T.

The Non-formation of an *o*-Tolylhydrazone of Lactose, an Affirmation of its Molecular Structure, and on its Indirect Identification. A. W. VAN DER HAAR (*Rec. trav. chim.*, 1918, **37**, 251—253).—The disaccharides, sucrose, maltose, and lactose, and the trisaccharides, trehalose and raffinose, do not yield *o*-tolylhydrazones. This result is considered to support Fischer's view as to the constitution of lactose (compare *Ber.*, 1893, **26**,

2400). Sugars, which on hydrolysis yield galactose, may be detected by hydrolysing them and preparing galactose-*o*-tolyl-hydrazone (compare A., 1917, ii, 515) from the hydrolysate.

W. G.

Constitution of ⸱the Disaccharides. II. Lactose and Melibiose. WALTER NORMAN HAWORTH and GRACE CUMMING LEITCH (T., 1918, **113**, 188—199).—A study of the methylation of lactose, and of the hydrolysis of the product, has provided evidence which, with the previously known reactions of the disaccharide, is sufficient to establish the exact constitution of lactose and to make practically certain the structure of melibiose. Methylation is effected by means of methyl sulphate and sodium hydroxide at 30—40°, and the *heptamethyl methyllactoside* so formed yields tetramethylgalactose and a trimethylglucose on hydrolysis with 5% hydrochloric acid at 98°, these being separated by taking advantage of the fact that the former gives an insoluble anilide (Irvine, T., 1910, **97**, 1454). The trimethylglucose is stable towards permanganate, and so must be a γ-oxide; it reduces Fehling's solution, it does not form an osazone, and is not identical with Purdie and Bridgett's compound (T., 1903, **83**, 1039), which has the group –$CH_2 \cdot OH$ at the end of the chain, thus limiting it to one of two isomerides.

Now, since lactose forms an osazone, and lactobionic acid yields galactose and gluconic acid on hydrolysis, it follows that the reducing group of the glucose residue is free and the adjacent hydroxyl also. The next hydroxyl must also be free, since the galacto-arabinose obtained by the degradation of lactose (Ruff and Ollendorff, A., 1900, i, 476) also forms an osazone. At the fourth carbon atom of the glucose fragment there can be no hydroxyl group, for the above trimethylglucose is γ-oxidic, and as this ether does not contain a free hydroxyl group in the sixth position, it follows that the attachment of the galactose residue to the glucose system in lactose is at the fifth carbon atom. Thus, formula I represents lactose, and, consequently, melibiose is most probably represented by formula II.

$$CH_2 \cdot OH$$

CH——O——CH	CH——O——CH$_2$
CH·OH CH	CH·OH CH·OH
CH·OH CH·OH	CH·OH CH
CH CH·OH	CH CH·OH
CH·OH CH·OH	CH·OH CH·OH
CH$_2$·OH	CH$_2$·OH CH·OH
(Galactose residue.) (Glucose residue.)	
(I.)	(II.)
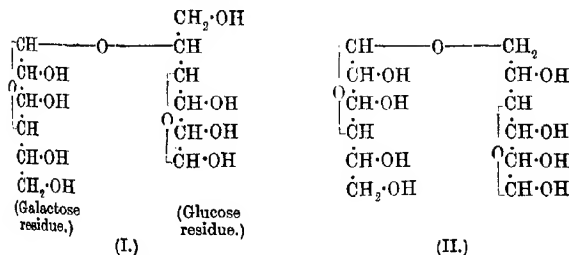
This conclusion possesses the novel feature that a disaccharide is represented as having a branched chain. It is probable that the

existence of four reducing disaccharides containing two glucose residues is to be explained on similar grounds.

[For experimental details and other arguments, see the original.]
J. C. W.

A Reinvestigation of the Cellulose–Dextrose Relationship.

MARY CUNNINGHAM (T., 1918, **113**, 173—181).—The commonly accepted opinion that cellulose is a polydextrose anhydride is based on the assumption that cellulose is quantitatively resolved into dextrose on hydrolysis. The evidence in favour of this view is not based on the isolation of dextrose in quantitative yield, but on the rotation and reducing power of the solutions (compare Willstätter and Zechmeister, A., 1913, i, 955).

It is now shown that such evidence is inadmissible, for cotton and esparto celluloses, although widely different types, give identical optical data on hydrolysis by 40% hydrochloric acid, and an acid of this concentration is known to produce constitutional changes in the simple hexoses themselves. Actual isolation and identification of the products of the hydrolysis, or simple derivatives of them, should be aimed at in such problems.

The author has therefore studied the hydrolysis of cotton and esparto cellulose by sulphuric acid dihydrate and 40% hydrochloric acid, and finds that the products are really esters of polysaccharides which contain acidic hydroxyl groups, and consequently may be isolated as barium or lead salts. No dextrose could be detected, even if the salts were heated with dilute acids, this having the effect of producing further condensation and not hydrolysis. Esparto cellulose is largely furfuroid, but the yield of furfuraldehyde obtained on distilling the diluted solution of the material is lower the longer the diluted liquid is kept, this pointing again to further condensation and not to hydrolysis.   J. C. W.

Esparto Cellulose and the Problems of Constitution.

CHARLES FREDERICK CROSS and EDWARD JOHN BEVAN (T., 1918, **113**, 182—187. Compare preceding abstract).—Esparto cellulose differs from other celluloses in giving rose-red colorations with aromatic amines and in yielding a constant high proportion (12·5%) of furfuraldehyde when decomposed by acids. It is isolated from the raw material by digesting with 17% of its weight of 3—4% sodium hydroxide at 130°, which treatment has no influence on the furfuroid content. The liquor contains, however, a colloidal furfuroid which yields as much as 50% of furfuraldehyde on boiling with hydrochloric acid. When the purified cellulose is treated with "mercerising soda" (17·5% sodium hydroxide) at 15—20°, or acetylated, or left with sulphuric acid di- or tri-hydrate, or when the concentrated, colloidal furfuroid is digested with sulphuric acid dihydrate, the furfuroid groups suffer change, for the yield of furfuraldehyde from the various products is reduced to about 7·5—8·5%. This renders doubtful the usual assumption that the furfuroids of esparto are pentosans, and coupled with the fact that

cellulose yields stable sulphates and chlorides, which hexoses and their anhydrides do not, it follows that the conception of cellulose as a complex of actual hexosan, or hexosan–pentosan, groups is no longer tenable. J. C. W.

Constitution of the Pectin Substances. TH. VON FELLENBERG (*Biochem. Zeitsch.*, 1918, **85**, 118—161. Compare A., 1915, i, 705, 774).—The pectin substances were obtained from various fruits by treating the same first with hot alcohol and then with water at 125°. To the aqueous extract were then added alcohol and hydrochloric acid, and the pectin was precipitated as a gelatinous mass. On treatment with sodium hydroxide, scission of methyl alcohol to the extent of 7—11% takes place, and the pectin is converted into pectic acid. Pectin is soluble in water, and various preparations yielded furfuraldehyde corresponding with between 35% and 46% of arabinose and 6% and 10% of methyl pentose.

Pectic acid is sparingly soluble in hot water, giving colloidal solutions which are flocculated by salts.

Experiments on fruit jellies indicate that these owe their existence to the combined presence of sugar, pectin, and salts. The so-called bassorin of gum tragacanth also yields methyl alcohol on treatment with sodium hydroxide, and is converted into bassoric acid, which differs from pectic acid in that it is readily soluble in water. S. B. S.

Mechanism of the Electrochemical Synthesis of Carbamide. FR. FICHTER (*Zeitsch. Elektrochem.*, 1918, **24**, 41—45).—The author has carried out a number of experiments with the object of explaining the mechanism of the formation of carbamide at the anode in the electrolysis of a solution of ammonium carbonate (Drechsel, A., 1881, 192). It is shown that this synthesis can also be effected by the action of oxidising agents (ozonised oxygen, hydrogen peroxide, or calcium permanganate) on a concentrated solution of ammonium carbonate in concentrated ammonia. The hypothesis previously put forward to explain the reaction is therefore inadequate. The main change in all the reactions is the oxidation of ammonia to ammonium nitrite and nitrate. During the oxidation, at the anode or at the surface of contact with the oxidising agent, heat is set free, which is removed by external cooling to prevent loss of ammonia. This local elevation of temperature converts a portion of the ammonium carbonate into carbamide. The anodic and chemical formation of carbamide are therefore fundamentally the same as the formation in the living organism. The formation of carbamide from ammonium carbonate or ammonium carbamate is expressed by the equations

$$NH_2 \cdot CO_2 \cdot NH_4 + H_2O \rightleftharpoons (NH_4)_2CO_3 \rightleftharpoons CO(NH_2)_2 + 2H_2O.$$
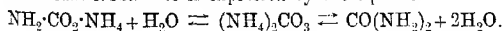
At and above 135°, ammonium carbamate cannot exist in the presence of water, consequently at this temperature and above only the right half of the equation comes into operation; with falling temperature, the equilibrium shifts to the right. Below 135°, an

increasing proportion of the ammonium carbonate is converted into the more stable carbamate, and is therefore withdrawn from the reaction if the carbonate is not stabilised by the addition of water. The lower the temperature the greater is the amount of water necessary to make the formation of carbamide possible. The best solution for carbamide formation consists of 1 mol. of ammonium carbamate and 9 mols. of water, and on the assumption that the local temperature elevation does not exceed 100°, calculations of the yield of carbamide do not contradict the hypothesis, inasmuch as the actual yields are much below the calculated values. The results show that ammonium carbonate only can be directly converted into carbamide.   J. F. S.

The Direct Conversion of Nitriles into Esters. L. Spiegel [with H. Szydlowsky] (*Ber.*, 1918, **51**, 296—298).—The authors have found that the best conditions for the preparation of ethyl esters from nitriles are, generally speaking, treatment with one molecular proportion of concentrated sulphuric acid and ten of alcohol, at 130—140°, in a sealed tube. The lower aliphatic nitriles give equally good results, and in the aromatic series the only hindrance which is recorded is a methyl group in the ortho-position.
                                          J. C. W.

The Three Trichlorobenzenes and their Reaction with Sodium Methoxide. A. F. Holleman (*Rec. trav. chim.*, 1918, **37**, 195—204).—1 : 2 : 3-Trichlorobenzene, m. p. 52°, was prepared from 2 : 6-dichloro-4-nitroaniline by the following series of actions, $NO_2 \cdot C_6H_2Cl_2 \cdot NH_2 \longrightarrow C_6H_2Cl_3 \cdot NO_2 \longrightarrow C_6H_2Cl_3 \cdot NH_2 \longrightarrow C_6H_3Cl_3$, the intermediate products not being isolated. 1 : 3 : 5-Trichlorobenzene, m. p. 63°, was prepared from the same starting material by the series of actions $NO_2 \cdot C_6H_2Cl_2 \cdot NH_2 \longrightarrow C_6H_3Cl_2 \cdot NO_2 \longrightarrow C_6H_3Cl_2 \cdot NH_2 \longrightarrow C_6H_3Cl_3$. The three trichlorobenzenes were heated separately in sealed tubes at 180° with a solution of sodium methoxide, the 1 : 2 : 3-isomeride yielding 2 : 3-dichlorophenol, 2 : 6-dichlorophenol, and a certain amount of the corresponding anisoles; the 1 : 2 : 4-isomeride yielded 2 : 5-dichlorophenol with a small amount of 2 : 5-dichloroanisole, and the 1 : 3 : 5-isomeride yielded 3 : 5-dichloroanisole as the principal product with a small amount of 3 : 5-dichlorophenol. The velocity of reaction of the three trichlorobenzenes with sodium methoxide is much greater than that of the three dichlorobenzenes with the same reagent, the 1 : 3 : 5-isomeride being the most easily attacked.   W. G.

A Reaction of Aromatic Nitro-compounds. S. C. J. Olivier (*Rec. trav. chim.*, 1918, **37**, 241—244).—The author has examined the behaviour of twelve aromatic compounds having one or more nitro-groups in the benzene nucleus, and finds that in benzene solution they all give with aluminium bromide an orange-red coloration which disappears on the addition of water. It is suggested that the coloration is due to the loose combination of the aluminium bromide with the nitro-group. In the absence of a solvent or

ın replacing the benzene by carbon disulphide, the characteristic ;oloration is not given in most cases. W. G.

Preparation of Derivatives of the 9 : 10-Dichloroan-thracenes. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., ?96019; from *Chem. Zentr.*, 1917, i, 460).—The 9 : 10-dichloro-ınthracenes combine directly with nitric acid in indifferent, cold media, giving well-defined, crystalline products, probably of the formula $C_6H_4 \underset{\diagdown CCl(NO_2)}{\overset{\diagup CCl(OH)}{<}} > C_6H_4$. These decompose most readily, especially on warming with concentrated sulphuric acid, or organic solvents or diluents, giving anthraquinones.

Thus, 9 : 10-dichloroanthracene itself gives the above *additive* compound, which crystallises in very pale yellow needles, and decomposes at 90—95° into anthraquinone. 2 : 9 : 10-Trichloroanthracene yields a similar nitric acid compound, which gives 2-chloroanthraquinone, m. p. 204—206°, on decomposition. J. C. W.

Limits of Accuracy of Holleman's Method of Determining the Composition of a Mixture of Two or Three Isomerides. JOSEPH B. NICHOLS (*J. Amer. Chem. Soc.*, 1918, **40**, 400—403).— A method, proposed by Holleman (Die direkte Einführung von Substituenten in den Benzolkern, 1910), for the estimation of the components in a mixture of three isomerides has been submitted to examination by experiments with certain mixtures of *o*-, *m*-, and *p*-nitroanilines.

The results obtained show that the addition of *o*-nitroaniline in small quantities lowers the eutectic temperature (86·7°) which is characteristic of the binary system *m*-nitroaniline + *p*-nitroaniline ;o an extent which is nearly proportional to the amount of *o*-nitro-aniline added. It is further found that the freezing point of *p*-nitroaniline is depressed by *m*-nitroaniline to an extent which is not appreciably altered when a small proportion of the *m*-nitro-aniline is replaced by *o*-nitroaniline. By combining observations of the freezing point and the eutectic point, it is thus possible to estimate the proportion of *o*-, *m*-, and *p*-nitroanilines in certain mixtures of these isomerides.

The *p*-nitroaniline branch of the freezing curve for mixtures of *m*- and *p*-nitroaniline has been determined. The temperature falls from 146·99° to 97·21° when the addition of the meta-compound amounts to 48·9%. [Compare also *Ind.*, May.] H. M. D.

New Method of Preparation of Monomethylaniline and Dimethylaniline by Catalysis. ALPHONSE MAILHE and F. DE GODON (*Compt. rend.*, 1918, **166**, 467—469).—Aluminium oxide is the most satisfactory catalyst for the dehydration. If the vapours of aniline and methyl alcohol in slight excess are passed over this oxide at 400—430°, a mixture of methyl- and dimethyl-anilines is obtained, and the methylation may be completed by further passage of the methylaniline and methyl alcohol over the catalyst. [See also *Ind.*, May.] W. G.

n*

New Preparation of the Methyltoluidines by Catalysis. ALPHONSE MAILHE and F. DE GODON (*Compt. rend.*, 1918, **166**, 564—566).—The method used for the preparation of methyl- and dimethyl-anilines (compare preceding abstract) is equally satisfactory for the preparation of the methyltoluidines. If the vapours of either *o*-, *m*-, or *p*-toluidine and methyl alcohol are passed over aluminium oxide at 350—400°, a mixture of methyl- and dimethyl-toluidines is obtained. A second treatment converts this mixture entirely into the tertiary base. [See also *Ind.*, May.]   W. G.

Separation of Secondary Arylamines from Primary Amines. TUDOR WILLIAMS PRICE (*J. Soc. Chem. Ind.*, 1918, **37**, 82—84T).—The method depends essentially on the fact that the sulphates of primary amines are insoluble in the free bases, whilst those of *sec.*- and *tert.*-amines are soluble in an excess of the free amines (compare Gnehm and Blumer, *ibid.*, 1899, **18**, 129). It is particularly adaptable to the recovery of unchanged base from the mixture obtained by heating an aromatic amine with an alcohol in the presence of a condensing agent, for the quantity of primary amine to be removed is usually not excessive.

The mixture is treated with sufficient concentrated sulphuric acid to combine with the primary amine (determined by titration), when this is almost completely precipitated as sulphate. A repetition of the process may be advisable. Considerable quantities of the alkylated base are carried down with the precipitate, so this is economically washed with the alcohol employed in the reaction. The recovered alcohol and sulphate may then be used in a second charge.   J. C. W.

Production of Aromatic Selenium Compounds. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P., 299510; from *Chem. Zentr.*, 1917, ii, 509—510).—Organic selenium compounds can be prepared by treating such substances as aniline, acetanilide, phenol, salicylic acid, and nitrophenol with a solution of selenium or selenium dioxide in sulphuric acid at low temperature. The product from acetanilide forms colourless crystals, m. p. approx. 260°; colourless products were also obtained from phenol, salicylic acid, and resorcinolarsinic acid, whereas aniline sulphate yielded an almost black powder and *o*- and *p*-nitrophenols yellow products. The *compound*, needles, m. p. 260° (decomp.), produced from *p*-acetylaminophenetidine had the composition

$$(OEt \cdot C_6H_3 \cdot NHAc)_3SeSO_4H, H_2O,$$

whilst antipyrine yielded a *diantipyryl selenide*, $(C_{11}H_{11}ON_2)_3Se$, colourless needles, m. p. 240° (decomp.).   D. F. T.

The Ternary System: Phenol–Acetamide–Ethyl Alcohol and the Binary System: Phenol–Benzamide. Theory of Recrystallisation. ROBERT KREMANN and MAX WENZING (*Monatsh.*, 1918, **38**, 479—500).—When heated with phenol, acetamide and benzamide are converted into phenyl acetate and benzoate respectively, with liberation of ammonia. Doubtless intermediate

additive compounds are formed, because the fusion curve for mixtures of phenol and acetamide shows a maximum m. p. $40\cdot8°$ at the composition $CH_3\cdot CO\cdot NH_2,2C_6H_5\cdot OH$, this result being interpreted as an indication of the presence of a free valency electron at the carbonyl and also at the amino-group of the amide. Benzamide apparently has a weaker affinity than acetamide towards phenol, the fusion curve for benzamide–phenol showing the occurrence of a compound $C_6H_5\cdot CO\cdot NH_2,2C_6H_5\cdot OH$, but the molten compound is dissociated to such an extent that the maximum m. p. is not observable.

The failure to obtain the compound $CH_3\cdot CO\cdot NH_2,2C_6H_5\cdot OH$ by recrystallisation of a mixture of the two constituents from alcohol is attributed to the relatively low m. p. of the compound, which in the presence of a third substance, such as alcohol, may fall well below the ordinary temperature. A theoretical consideration is "iven of the conditions of equilibrium in a ternary system such as ,henol–acetamide–alcohol, the assumption being made that there is ,o further formation of compounds, either binary or tertiary.

D. F. T.

Solubility of Salts of Nitrophenols in Mixtures of Alcohol nd Water. W. M. FISCHER (*Zeitsch. physikal. Chem.*, 1918, **92,** 81—599).—The solubility of sodium picrate, $C_6H_2(NO_2)_3\cdot ONa,H_2O$, n mixtures of water and ethyl alcohol at 0° and 25° varies with he composition of the solvent in a remarkable way, in that the urve shows a maximum and two minima. The maximum occurs it about 50% of alcohol by volume and the minima at about 25% ind 95—99% respectively.

The anomalous form of the curve has led to the investigation of the solubility of other salts of nitrophenols, including potassium picrate, barium picrate, the sodium salts of p-nitrophenol, 2:4-dinitrophenol, and 2-chloro-4-nitrophenol, and also barium dinitrosalicylate. The results indicate that the curve is of the same type in all these cases, showing a maximum and two minima. It is suggested that the anomalous solubility curve is due to the existence of two isomeric forms of the salts, the equilibrium between which is displaced as the proportion of alcohol to water is changed. As evidence in support of this view, preliminary measurements of the extinction coefficients for solutions of salts of the nitrophenols in mixtures of ethyl alcohol and water are adduced which show that the absorption is not by any means a linear function of the composition of the solvent.

The solubility curves for potassium picrate and the sodium salt of 2:4-dinitrophenol exhibit a maximum in mixtures of acetone and water and a minimum in mixtures of methyl alcohol and water.

H. M. D.

The Salts of the Complex Acid : Catechol–Boric Acid. J. BÖESEKEN [with A. OBREEN and (MLLE.) A. VAN HAEFTEN] (*Rec. trav. chim.*, 1918, **37,** 184—194).—The two metallic and the ammonium salts were prepared by shaking concentrated solutions

of boric acid, catechol, and the respective hydroxide together in the molecular proportions $1:2:1$. The three salts separated in the form of white leaflets. The salts of the organic bases were similarly prepared, the salts crystallising in needles. The following salts were prepared: *ammonium* salt, $(C_6H_4O_2)_3B_2O_4(NH_4)_2$; *potassium* salt, $(C_6H_4O_2)_3B_2O_4K_2$ or $(C_6H_4O_2)_3B_2O_4H_2K_2$; *rubidium* salt, analytical results not satisfactory; *aniline* salt, constitution not settled; *dimethylaniline* salt, $(C_6H_4O_2)_3BO_4H_2(C_6H_4\cdot NMe_2),5H_2O$ [?]; p-*chloroaniline* salt, $(C_6H_4O_2)_3B_3O_3(C_6H_4Cl\cdot NH_2)_3,4H_2O$ [?].

W. G.

Methylation with Methyl Sulphate, Hydrolysis of Methyl Sulphate with Aqueous Alkali and Water in a Heterogeneous System, and a Case of Potassium Catalysis.

Alfons Klemenc [with Emma Edhofer] (*Monatsh.*, 1918, **38**, 553—580). —The unequal behaviour of potassium and sodium salts has occasionally been observed, for example, in the better yield of methyl benzoate obtained by the reaction of methyl sulphate with potassium benzoate than with sodium benzoate (Graebe, A., 1905, i, 678), and the better methylation of potassium benzoate by potassium methyl sulphate than by sodium methyl sulphate. It is now shown that in the methylation of phenolic hydroxyl, for example, in quinol or resorcinol, the use of potassium hydroxide gives much poorer yields than sodium hydroxide. Physico-chemical considerations exclude the possibility that the difference is to be attributed to the different rates of diffusion of the two hydroxides from one phase to another in the heterogeneous system, and indicate that the hydrolysis occurs in a homogeneous system containing the dissolved ester. Any possible difference in the solubility of methyl sulphate in aqueous solutions of the respective alkalis is insufficient to account for the inequality in their effect. The probable explanation is that potassium hydroxide effects a more rapid hydrolysis of methyl sulphate than sodium hydroxide of equivalent concentration, on account of a catalytic influence of the undissociated potassium hydroxide molecules, in confirmation of which it is found that the addition of potassium chloride to a solution of sodium hydroxide raises the hydrolysis constant, whereas the addition of sodium chloride depresses it; on the other hand, the addition of potassium chloride to potassium hydroxide solution also depresses the hydrolysis constant. The conclusion is therefore drawn that during the methylation of a phenol, the undissociated phenoxide and the hydroxyl ions react concurrently and independently with the methyl sulphate, and that the poorer yield of methoxy-derivative obtained with the use of potassium hydroxide is due to the catalytic acceleration of the latter reaction.

D. F. T.

6-Thiol-β-naphthol.

Th. Zincke and R. Dereser (*Ber.*, 1918, 51, 352—360).—The preparation of 6-thiol-β-naphthol and its more important derivatives is described (compare the 4- and 5-thiol-β-naphthols, A., 1915, i, 135, 531).

β-Naphthol-6-sulphonic acid is converted by means of ethyl chloroformate into *sodium 2-ethylcarbonatonaphthalene-6-sulphonate*, pearly leaflets, and this into the sulphonyl *chloride*, m. p. 118°, and then into 2-*ethylcarbonatonaphthalene-6-sulphon-anilide*, $CO_2Et\cdot O\cdot C_{10}H_6\cdot SO_2\cdot NHPh$, bundles of needles, m. p. 130°, which may be hydrolysed to *β-naphthol-6-sulphonanilide*, m. p. 105°. The sulphonyl chloride is reduced by means of zinc dust and hydrochloric acid to 2-*ethylcarbonatonaphthalene-6-thiol*,

$$CO_2Et\cdot O\cdot C_{10}H_6\cdot SH,$$
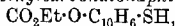
which crystallises in glistening scales, m. p. 87°, and may be reconverted into the sulphonyl chloride by treatment with chlorine. The thiol forms an *acetate*, m. p. 95°, and may be oxidised by alcoholic ferric chloride to *di-2-ethylcarbonato-6-naphthyl disulphide*, $(CO_2Et\cdot O\cdot C_{10}H_6)_2S_2$, glistening scales, m. p. 127°. It also reacts with methyl sulphate to form 2-*ethylcarbonato-6-naphthyl methyl sulphide*, $CO_2Et\cdot O\cdot C_{10}H_6\cdot SMe$, which crystallises in long, glistening needles, m. p. 97°, reacts with chlorine to form an obscure *tetrachloride,* m. p. 167—172°, and may be oxidised by means of hydrogen peroxide to the corresponding *sulphoxide*,
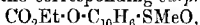
$$CO_2Et\cdot O\cdot C_{10}H_6\cdot SMeO,$$

scales, m. p. 67°, or *sulphone*, $CO_2Et\cdot O\cdot C_{10}H_6\cdot SMeO_2$, scales, m. p. 98°.

6-*Thiol-β-naphthol* is obtained by hydrolysing the above ethyl carbonatonaphthalenethiol. It crystallises in odourless leaflets, m. p. 137°, and forms a *diacetate*, m. p. 107°. The corresponding disulphide, methylthiol, and its sulphoxide and sulphone, are also prepared by hydrolysing the ethylcarbonato-compounds. *Di-β-naphthol-6 disulphide* forms colourless leaflets, m. p. 220—221°, and yields a *diacetate*, m. p. 167—168°; *β-naphthol-6 methyl sulphide* crystallises in silvery leaflets, m. p. 121°. forms an *acetate,* m. p. 74°, may be methylated to 2-*methoxy-6-naphthyl methyl sulphide*, m. p. 105—106°, and reacts with bromine to form 1:5-*dibromo-β-naphthol-6 methyl sulphide*, leaflets, m. p. 194—195° (*acetate*, m. p. 145°), and the corresponding *dibromide*,

$$OH\cdot C_{10}H_4Br_2\cdot SMeBr_2,$$
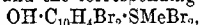
reddish-brown crystals; *β-naphtholmethyl-6-sulphoxide*,
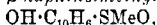
$$OH\cdot C_{10}H_6\cdot SMeO.$$

has m. p. 164—165°, and the *sulphone*, $OH\cdot C_{10}H_6\cdot SMeO_2$, has m. p. 151—152°, and forms an *acetate*, m. p. 145—146°, and *methyl ether*, m. p. 143—144°.

β-*Naphthol-6-sulphinic acid*, $OH\cdot C_{10}H_6\cdot SO_2H$, is prepared by adding a mixture of 2-ethylcarbonatonaphthalene-6-sulphonyl chloride and sodium hydrogen carbonate to a warm solution of sodium sulphite. It crystallises in leaflets, decomp. 120—125°, and forms a methyl ester and methyl ether of this, which are identical with the above β-naphthol-6-methylsulphone and its methyl ether.

J. C. W.

Preparation of 1 : 8-Dihydroxyanthranol. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 296091; from *Chem. Zentr.*, 1917, i, 351).—1:8-*Dihydroxyanthranol*, m. p. 178—180°, a valuable

agent in cases of psoriasis and other skin diseases, is prepared by the reduction of $1:8$-dihydroxyanthraquinone by means of zinc and an acid.   J. C. W.

Preparation of Acyl Derivatives of Aminonaphthols and their Sulphonic Acids. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P., 295767 and 296446; from *Chem. Zentr.*, 1917, i, 293, 546).—Aminonaphthols and their sulphonic acids are treated with 2-hydroxy-3-naphthoyl chloride or its acetyl derivative, giving naphthoylamino-compounds which have a great affinity for cotton and silk. Thus, 2-amino-5-naphthol-7-sulphonic acid yields 2-2'-*hydroxy-3'-naphthoylamino-5-naphthol-7-sulphonic acid,* as an almost colourless, crystalline mass, which is fixed by cotton in an alkaline solution or by silk in acetic acid solution, and may be coupled with diazonium salts on the fibre. 2-2'-*Hydroxy-3'-naphthoylamino-8-naphthol-6-sulphonic acid,* 1-2'-*hydroxy-3'-naphthoylamino-8-naphthol-3:6-disulphonic acid,* 1-2'-*acetoxy-3'-naphthoylamino-7-naphthol,* m. p. 198—200°, and 1-2'-*hydroxy-3'-naphthoylamino-7-naphthol,* m. p. 198—200°, are pale grey, crystalline masses or powders.   J. C. W.

d-Benzylidenecampholic Acid. HANS RUPE and ALFRED BLECHSCHMIDT (*Ber.*, 1918, **51**, 170—180).—A revision of the work on the action of hydrobromic acid on *d*-benzylidenecamphor described by Haller and Minguin (A., 1900, i, 452).

Benzylidenecamphor is conveniently prepared by treating camphor with sodium in toluene solution, and then adding benzaldehyde and gently boiling in a current of hydrogen. When heated in a pressure bottle at 100° with a solution of hydrogen bromide in slightly diluted acetic acid, saturated at 0°, it is converted into a crystalline acid mixed with a viscous substance. These are separated by boiling with magnesium oxide and water, the viscous substance being chiefly a non-acidic wax, and not benzylidenecampholic acid, as Haller and Minguin suggested. The acid recovered from the magnesium salt is the phenylhydroxy-homocampholic acid described by the French workers, but as it loses water readily on boiling with formic acid, it is supposed to be represented more correctly by the alternative formula,

$$CO_2H\cdot C_8H_{14}\cdot CH(OH)\cdot CH_2Ph.$$
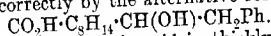
It crystallises from diluted acetic acid in thickly interwoven, stout needles, m. p. 206°, and forms an *ethyl* ester, long needles, m. p. 104°.

d-Benzylidenecampholic acid, $CO_2H\cdot C_8H_{14}\cdot CH\!:\!CHPh$, is the product of the action of formic acid on the hydroxy-acid. It is purified by distillation, followed by crystallisation from acetic acid (4 acid to 1 water), and is then obtained in asbestos-like masses, m. p. 124—125°, b. p. 228°/11 mm., which yield benzoic and camphoric acids on oxidation with permanganate. The *methyl* ester forms large, star-like groups of needles, m. p. 97·5—98°, and the *ethyl* ester small, glistening prisms, m. p. 95—97°; these are prepared from the chloride, which is obtained by the action of

thionyl chloride. The acid may be hydrogenated in the presence of nickel or colloidal palladium, d-*benzylcampholic acid* being obtained in slender needles, m. p. 119—119·5°, and its *methyl* ester in long, flat needles, m. p. 44°, b. p. 196—197°/13 mm. It also combines with bromine to form *αβ-dibromobenzylcampholic acid*, $CO_2H \cdot C_8H_{14} \cdot CHBr \cdot CHPhBr$, long needles, m. p. 161°, and with hydrogen bromide in glacial acetic acid to form *α-bromobenzyl-ampholic acid*, $CO_2H \cdot C_8H_{14} \cdot CHBr \cdot CH_2Ph$, which crystallises in groups of spiky needles, m. p. 139°, and is also produced in excellent yield when benzylidenecamphor is left for four months with a saturated solution of hydrogen bromide in glacial acetic acid.

J. C. W.

Some Stereoisomerides of Benzylidenementhone Hydrocyanide [Phenylmenthylacetonitrile; Phenylmenthylcyanomethane].

EYVIND BOEDTKER (*Bull. Soc. chim.*, 1918, [iv], **23**, 34—70).—The author has isolated seven stereoisomeric phenylmenthylacetonitriles from the products of the action of potassium cyanide on benzylidenementhone hydrochloride in alcoholic solution (compare A., 1916, i, 51). They have respectively the following properties: (1) slender, yellow needles, m. p. 193°, $[a]_D^{24} -83°23'$ (in benzene); (2) colourless prisms, m. p. 158°, inactive; (3) colourless prisms, m. p. 148°, $[a]_D^{26} +78°7'$ (in benzene); (4) colourless plates, m. p. 124°, $[a]_D^{26} -53°32'$; (5) silky needles, m. p. 183°, $[a]_D^{26} -58°51'$; (6) slender needles, m. p. 201°, inactive; (7) long needles, m. p. 205°, inactive. If in the preparation of these compounds the reagents are only heated in boiling alcoholic solution for one hour, the main product is the isomeride (1), but if the time of heating is prolonged or a little potassium hydroxide is introduced, the main product is the stable stereoisomeride (6), m. p. 201°.

W. G.

A New Synthesis of Tropic Acid.

E. MÜLLER (*Ber.*, 1918, **51**, 252—255).—All syntheses of tropic acid so far attempted have started from compounds, such as acetophenone, in which the $:CPh \cdot CH_2 \cdot$ grouping is pre-existent. None of the successful methods can be regarded as simple, but the other alternative, using a compound with the $\cdot CHPh \cdot CO_2R$ grouping, is now found to be a most convenient synthesis, which may perhaps be applied to substituted tropic acids.

Ethyl phenylacetate and ethyl formate are condensed in the presence of sodium to form the well-known mixture of desmotropic ethyl formylphenylacetates, and this mixture is reduced by means of aluminium amalgam in moist ether. About half of the formylphenylacetate combines with the sludge of aluminium hydroxide, and can only be recovered after shaking this with dilute sulphuric acid. The ethyl tropate present in the ethereal solution is hydrolysed by warm barium hydroxide solution.

J. C. W.

The Benzoylated Cyanohydrins from Aldehydes and Ketones, and the Corresponding Amides and Acids.

J. ALOY and CH. RABAUT (*Bull. Soc. chim.*, 1918, [iv], **23**, 98—101).—By

the methods previously described (compare A., 1912, i, 462; 1913, i, 620, 728; 1916, i, 263), the following benzoylcyanohydrins and the corresponding amides and acids have been obtained.

α-*Benzoyloxy-γ-phenyl-Δβ-butenonitrile*, $CHPh:CH\cdot CH(OBz)\cdot CN$, m. p. 66—67°, gives the *amide*, $CHPh:CH\cdot CH(OBz)\cdot CO\cdot NH_2$.

α-*Benzoyloxy*-p-*isopropylphenylacetonitrile*,
$$CHMe_2\cdot C_6H_4\cdot CH(OBz)\cdot CN,$$
m. p. 65°, gives the corresponding *amide*, m. p. 182°, which on hydrolysis yields p-*iso*propylphenylglycollic acid.

1-*Benzoyloxycyclopentane*-1-*carboxylonitrile*, $OBz\cdot C_5H_8\cdot CN$, m. p. 52—53°, giving the *amide*, $OBz\cdot C_5H_8\cdot CO\cdot NH_2$, m. p. 111—112°.

The cyanohydrin from heptaldehyde was not isolated, but the oily product, when hydrolysed with dilute sulphuric acid, yielded the *amide*, $CH_3\cdot [CH_2]_5\cdot CH(OBz)\cdot CO\cdot NH_2$, m. p. 104—105°.

αβ-*Dibenzoyloxysuccinonitrile*, $OBz\cdot CH(CN)\cdot CH(OBz)\cdot CN$, m. p. 195—196°, did not yield an amide, but tartaric acid was isolated from the products of hydrolysis.   W. G.

New Galloyl Derivatives of Dextrose and Comparison of them with Chebulic Acid. EMIL FISCHER and MAX BERGMANN (*Ber.*, 1918, **51**, 298—320).—Tri- and mono-galloylglucose have been obtained by means of glucosemonoacetone and glucosediacetone, a method by which partly acylated glucoses have been prepared already (A., 1916, i, 363). These derivatives have been compared very thoroughly with chebulic acid, which is known to yield gallic acid and dextrose on hydrolysis, but the conclusion is drawn that the acid is not related in structure to the galloylglucoses.

Glucosemonoacetone is treated with triacetylgalloyl chloride (this vol., i, 173) and quinoline, diluted with chloroform, and thus converted into *tri-triacetylgalloylglucosemonoacetone*,
$$CMe_2:C_6H_7O_6[CO\cdot C_6H_2(OAc)_3]_3,$$
which is a faintly reddish-yellow powder, $[\alpha]_D^{20} -66\cdot5°$ (in acetone). This is shaken at below 20°, in a current of hydrogen, with dilute sodium hydroxide, alcohol, and ether until solution takes place, when the mixture is exactly neutralised, giving *trigalloylglucosemonoacetone* as an amorphous, leafy mass, $[\alpha]_D^{21} -93\cdot3°$ (in acetone). Dilute solutions of the derivative give deep bluish-violet colours with ferric chloride, and form precipitates with gelatin, brucine, quinine, quinoline, and pyridine. The hydrolytic scission of the *iso*propylidene group is effected by means of 0·5*N*-sulphuric acid at 70°, *trigalloylglucose* being obtained as a tannin-like mass, $[\alpha]_D^{20} -118\cdot6°$ (in acetone), which is bitter and astringent in taste, whereas chebulic acid is sweet, and soluble in ice-cold water, whilst Chinese tannin is very sparingly soluble. A 10% alcoholic solution forms a jelly with 10% acoholic arsenic acid, and towards ferric chloride and bases it behaves like its acetone compound.
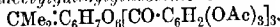
The methylcarbonato-derivative of galloyl chloride gives *tri-3:4:5-trimethylcarbonatobenzoylglucoseacetone*,
$$CMe_2:C_6H_7O_6[CO\cdot C_6H_2(O\cdot CO_2Me)_3]_3,$$
in amorphous flocks, $[\alpha]_D^{23} -56\cdot25°$ (in *s*.-tetrachloroethane).
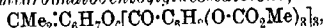
Similarly, the methyl ether yields *tri*-3:4:5-*trimethoxybenzoyl-glucoseacetone*, as a colourless powder, $[\alpha]_D^{20} - 89\cdot30°$ (in acetone), which does not give a colour with ferric chloride, and may be hydrolysed in the cold by means of concentrated hydrochloric acid dissolved in glacial acetic acid to form *tri*-3:4:5-*trimethoxy-benzoylglucose*, $C_6H_9O_6[CO\cdot C_6H_2(OMe)_3]_3$, $[\alpha]_D^{20} - 92\cdot99°$ (in acetone). The presence of two free hydroxyl groups in the glucose residue of this may be demonstrated by means of *p*-bromobenzoyl chloride, which, in the presence of quinoline, yields *di*-p-*bromo-benzoyltri*-3:4:5-*trimethoxybenzoylglucose*, a leafy mass, with $Br = 14\cdot17\%$. Trigalloylglucose reacts with diazomethane to give an indefinite methyl derivative, which also reacts with *p*-bromobenzoyl chloride, and as the product contains about $16\cdot8\%$ of bromine, it follows that at least two hydroxyl groups are left unattacked by the reagent. Chebulic acid behaves differently (see below).

Glucosediacetone yields *triacetylgalloylglucosediacetone*,
$$C_6H_7O_6(CMe_2)_2[CO\cdot C_6H_2(OAc)_3]_3,$$
a colourless flocks, $[\alpha]_D^{18} - 30\cdot13°$ (acetone), from which *galloylglucosediacetone*, $[\alpha]_D^{18} - 33\cdot82°$, *galloylglucosemonoacetone*, $[\alpha]_D^{20} - 20\cdot22°$, and *galloylglucose*, $C_6H_{11}O_6\cdot CO\cdot C_6H_2(OH)_3$, $[\alpha]_D^{18} + 46\cdot5°$ (alcohol), may be obtained as amorphous masses in the usual way. The behaviour of these towards the tannin reagents is described. Galloylglucose gives a deep blue colour with ferric chloride, but does not form precipitates with gelatin or bases. It is not identical with Feist's glucogallic acid (A., 1914, i, 195).

Chebulic acid, the eutannin of commerce, crystallises well from diluted acetone in needles. That it yields dextrose on hydrolysis with *N*-sulphuric acid has now been proved by the isolation of the osazone and by the fermentation method, but the cleavage proceeds at a much slower rate than is the case with the tri- and penta-galloylglucoses. A methylated chebulic acid may be obtained by the action of diazomethane (compare Richter, A., 1913, i, 989), but the product given by this when treated with *p*-bromobenzoyl chloride only contains about 9% of bromine. Chebulic acid therefore differs from trigalloylglucose. Furthermore, chebulic acid does not condense with acetone under the influence of hydrogen chloride, whereas tribenzoylglucose does so quite readily.

Tribenzoylglucose reacts in some way with diazomethane, but not to form a methylglucoside, for the product still reduces Fehling's solution. Apparently, also, it does not form an ether, for treatment with *p*-bromobenzoyl chloride, as above, indicates the presence of two free hydroxyl groups.　　　　J. C. W.

Partial Acylation of Polyhydric Alcohols and Sugars. IV. Derivatives of *d*-Glucose and *d*-Fructose. EMIL FISCHER and HARTMUT NOTH (*Ber.*, 1918, **51**, 321—352. Compare A., 1916, i, 363—365).—Hitherto, a tribenzoylglucose (*ibid.*, 364) and two stereoisomeric pentabenzoylglucoses (A., 1912, i, 888) have been

described. To these are now added a mono-, di-, and tetra-benzoyl-glucose, prepared by the application of the condensation products of dextrose with acetone. In the case of lævulose, a crystalline monogalloyl derivative is described, and some acyl derivatives of lævuloseacetone.

Benzoylglucosediacetone, which has now been obtained crystalline, with m. p. 63—64° (corr.), $[\alpha]_D^{18} -49.7°$ (compare A., 1915, i, 118), is left with $2N$-sulphuric acid and alcohol at 50°, and thus converted into *benzoylglucosemonoacetone*, $CMe_2{:}C_6H_9O_5{\cdot}OBz$, a crystalline mass, m. p. 195—197° (corr.), $[\alpha]_D^{20} +8.5°$ (alcohol), which does not reduce Fehling's solution. This is changed into tribenzoylglucosemonoacetone (A., 1916, i, 364) by means of benzoyl chloride and quinoline, and either of the benzoylglucose-acetones may be hydrolysed by means of a mixture of sulphuric and acetic acids at 70° to give *benzoylglucose*, $C_6H_{11}O_5{\cdot}OBz,H_2O$, which forms stout, glistening crystals, m. p. 104—106° (corr.), $[\alpha]_D^{21} +45.76°$, $+44.57°$ after twenty-four hours (in water), $[\alpha]_D^{20} +47.32°$, $+49.34°$ after twenty-four hours (in alcohol). This derivative has as great a reducing power as dextrose, and suffers no weakening of this property when heated at 100° for some hours. It may be condensed with acetone to form benzoylglucosediacetone again, and it reacts with phenylhydrazine in the cold to give a *phenylhydrazone*, pale yellow prisms, m. p. 146—147° (corr.), $[\alpha]_D^{20} +11.1°$ (in pyridine), whilst it yields glucosazone if warmed with this agent.

A substance, which was presumed to be a monobenzoylglucose, is the "vacciniin" isolated by Griebel from the whortleberry (A., 1910, ii, 440). Having been supplied with some residues by Griebel, the present authors have been able to confirm the fact that the above benzoylglucose does actually occur in the natural product. They have not succeeded in isolating the substance, but have obtained a pure specimen of benzoylglucoseacetone from the crude material.

Tetrabenzoylglucose is prepared by the action of silver carbonate on benzobromo-*d*-glucose (A., 1911, i, 803) in moist acetone. An amorphous product is obtained which exhibits mutarotation, and is obviously a mixture of stereoisomerides, but an individual substance, crystallising from much light petroleum in slender needles, m. p. 119—120° (corr.), $[\alpha]_D^{21} +70.6°$ (constant; alcohol), has been isolated. This forms an additive *compound* with pyridine in equimolecular proportions, which has m. p. 103—104° (corr.) and $[\alpha]_D^{24} +62.07°$ (in alcohol).

For the preparation of a dibenzoylglucose, partly acetylated derivatives prove to be the most suitable material. Glucosediacetone is treated with acetic anhydride and pyridine at 0°, and the *acetylglucosediacetone* so formed, m. p. 62—63°, $[\alpha]_D^{22} -31.5°$, which tastes very bitter and does not reduce Fehling's solution, is hydrolysed by a mixture of dilute sulphuric acid and alcohol at 50° to *acetylglucosemonoacetone*, m. p. 144—146° (corr.), $[\alpha]_D^{24} -6.27°$. This is treated with benzoyl chloride and pyridine, when *acetyldibenzoylglucoseacetone* is obtained, in elongated plate-

lets, m. p. 114—115° (corr.), $[a]_D^{25} -73\cdot98°$ (acetone). When left with a mixture of 5N-sulphuric acid and acetone at 90° in a pressure bottle, this loses not only the acetone residue, but the acetyl group as well, and *dibenzoylglucose* is formed. This crystallises from chlorobenzene in short needles or hexagonal platelets, 1. p. 145—146° (corr.), $[a]_D^{19}$ in alcohol, $+56\cdot2°$, $+66\cdot7°$ after six days, and reacts with p-bromobenzoyl chloride and pyridine to form *dibenzoyltri-p-bromobenzoylglucose*, $[a]_D^{9} +32°$.

Benzoylfructosediacetone is a crystalline substance, m. p. 07—108° (corr.), $[a]_D^{25} -161\cdot2°$, which neither reduces Fehling's solution nor reacts with phenylhydrazine, but yields *benzoylfructose-nonoacetone* when left with a mixture of acetone and N-hydro-chloric acid at 50°. This is a very bitter, crystalline material which sinters at about 185°, has m. p. 202—204° (corr.) and $a]_D^{15} -151\cdot64°$, and is very sparingly soluble in water. It yields *ribenzoylfructosemonoacetone*, an amorphous solid, which may be hydrolysed to an amorphous *tribenzoylfructose*, $[a]_D^{15} -249\cdot75°$, this being a powerful reducing sugar.

p-Bromobenzoylfructosediacetone crystallises in needles or prisms, m. p. 136—137° (corr.); *p-bromobenzoylfructosemonoacetone* has m. p. 222—225° (corr.); and *tri-p-bromobenzoylfructosemono-acetone* is a crystalline compound, with m. p. 142—143° (corr.), $[a]_D^{15}$ in acetone, $-365°$.

Acetylfructosediacetone crystallises from hot water in long, glistening needles, m. p. 76—77°, $[a]_D^{15} -176\cdot3°$; *acetylfructose-monoacetone* has m. p. 154—155° (corr.), $[a]_D^{19} -180\cdot6°$; *triacetyl-fructosemonoacetone* crystallises in groups of prisms, m. p. 99—101° (corr.), $[a]_D^{23} -134\cdot9°$; *benzoyldiacetylfructosemonoacetone*, m. p. 77—78°, $[a]_D^{22} -132\cdot5°$, is very sparingly soluble in water, but freely so in most organic solvents; *dibenzoylacetylfructosemonoacetone* crystallises in platelets, m. p. 108—109° (corr.), $[a]_D^{21} -269\cdot4°$, and has the same solubilities; and *di-p-bromobenzoylacetylfructose-monoacetone*, $CMe_2:C_6H_7O_6Ac(CO\cdot C_6H_4Br)_2$, forms large crystals, m. p. 146—147° (corr.), $[a]_D^{15} -288°$.

Fructosediacetone reacts with triacetylgalloyl chloride in the presence of quinoline, giving *triacetylgalloylfructosediacetone*, which crystallises in well-developed prisms or needles, m. p. 157—159° (corr.), $[a]_D^{28} -118\cdot17°$, and is hydrolysed by shaking with a mixture of alcohol and 2N-sodium hydroxide in an atmo-sphere of hydrogen to *galloylfructosediacetone*, a very bitter, astringent substance, m. p. 199—200° (corr.), $[a]_D^{18} -141\cdot24°$. The acetone residues may be removed in the usual way, and the pro-duct, *galloylfructose*, unlike the benzoyl derivatives, has been obtained crystalline. It forms masses of slender needles, decomp. 150—155°, $[a]_D^{19}$ in water, $-80\cdot4°$, and behaves like galloylglucose towards tannin reagents, except that it gives a jelly with alcoholic arsenic acid.　　　　　　　　　　　　　　　　　　　　J. C. W.

Preparation of a 1 : 5-Dihydroxynaphthalenedicarboxylic Acid. FRANZ VON HEMMELMAYR (D.R.-P., 296035; from *Chem, Zentr.*, 1917, i, 351. Compare A., 1917, i, 457).—1 :5-*Dihydroxy-*

naphthalenedicarboxylic acid is a yellow powder, m. p. about 300°
(decomp.), and forms colourless alkali salts, which exhibit blue
fluorescence in water and may be easily "salted out." The acid
and its salts combine with wool fibres, subsequent treatment with
chromic acid or chromates giving very pure brown tones.

J. C. W.

**The Mechanism of the Formation of Benzophenone by
the Friedel and Crafts' Reaction.** S. C. J. OLIVIER (*Rec. trav.
chim.*, 1918, **37**, 205—240).—A study of (1) the action of benzoyl
chloride on benzene in the presence of aluminium chloride in
benzene solution; (2) the action of benzoyl bromide on benzene in
the presence of aluminium bromide in benzene solution; (3) the
reaction (2), but in carbon disulphide as solvent. Reaction (1) is
unimolecular, and shows a slight but regular fall in the value of
K with the time. The presence of an excess of benzoyl chloride
is without influence on the reaction. One molecule of aluminium
chloride can only transform one molecule of benzoyl chloride, and
the action $COPhCl,AlCl_3 + C_6H_6 = COPh_2,AlCl_3 + HCl$ is not
reversible. Reaction (2) is also unimolecular, with a slight fall
in the value of K, but the velocity of reaction is much greater than
with the chlorides. With an excess of aluminium bromide, the
velocity of the reaction increases enormously, the excess of this
catalyst acting almost proportionately to its concentration. Cryo-
scopic measurements show that in benzene solution the compound
$COPh_2,AlBr_3$ easily forms associated molecules, the same being un-
doubtedly true of the compound $COPhBr,AlBr_3$, and these
associated molecules are notably more active than the unassociated
molecules. The reaction (3) in carbon disulphide solution may be
considered as bimolecular, with a fall in the value of K, an excess
of aluminium bromide again causing an enormous increase in the
velocity of reaction. The velocity constant also increases slightly
with an increase in the concentration of the benzene.   W. G.

Preparation of Triarylmethane Dyes, Fast to Light.
FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P., 295495;
from *Chem. Zentr.*, 1917, i, 150).—"Diarylindyl-dyes, which
contain an amino-, sulpho-, alkyloxy- or acyloxy-group in place of
the halogen atom in the para-position with regard to the methane
carbon atom, are treated with primary aromatic amines."
    The following intermediate compounds are mentioned:
p-methoxy-p'-dimethylaminobenzophenone, m. p. 133°, from
p-methoxybenzanilide and dimethylaniline; *p-hydroxy-p'-diethyl-
aminobenzophenone*, m. p. 188°, from *p*-amino-*p'*-diethylamino-
benzophenone, which is obtained from the nitro-compound, and
this from *p*-nitrobenzanilide and diethylaniline; *p-dimethylamino-
benzophenone-p'-sulphonic acid*, from the above amine by diazotisa-
tion, treatment with sulphurous acid and copper paste, and oxida-
tion of the sulphinic acid with permanganate; *p-amino-p'-dimethyl-*
amino-o'-methylbenzophenone, m. p. 151°, by the reduction of the

product obtained from *p*-nitrobenzanilide and dimethyl-*m*-toluidine; 1-*benzyl-2-methylindole*, b. p. 245°/16 mm., by melting the phenylbenzylhydrazone of acetone with zinc chloride.

J. C. W.

The Condensation of Aldehydes with ω-Bromoaceto-phenone, and some of the Compounds obtained thereby.

SVEN BODFORSS (*Ber.*, 1918, **51**, 192—214. Compare A., 1917, i, 223).—When ω-bromoacetophenone is treated with a solution of sodium ethoxide, it yields the *cis*- and *trans*-modifications of 2-bromo-3:4-oxido-3:5-diphenyltetrahydrofuran (A., 1913, i, 1219), but if certain aldehydes are present, condensation between the unlike molecules takes place, resulting in the formation of ethylene oxides, most probably according to the scheme COPh·CH₂Br +

$$CHPhO = COPh·CHBr·CHPh·OH = COPh·CH{\overset{CHPh}{\underset{O}{<}}} + HBr.$$

This condensation takes place particularly well if the aldehyde contains negative substituents, but negative results are usually given by aldehydes with positive substituents; thus, benzaldehyde, the nitrobenzaldehydes, *p*-chlorobenzaldehyde, bromo- and nitro-anisaldehydes, bromopiperonaldehyde, *m*-nitrocinnamaldehyde, cuminaldehyde, and terephthalaldehyde do react, whilst acet-aldehyde, *iso*butaldehyde, heptaldehyde, citraldehyde, anisaldehyde, piperonaldehyde, cinnamaldehyde, and *p*-toluraldehyde do not react with ω-bromoacetophenone. ω-Chloro-*p*-methoxyacetophenone, however, is of itself so very stable towards sodium ethoxide that even an aldehyde like anisaldehyde will condense with it in the above manner, although only slowly.

The following are new examples of the condensation of aldehydes with ω-bromoacetophenone in equimolecular proportions: *o*-nitrobenzaldehyde gives *benzoyl-o-nitrophenylethylene oxide*, rectangular prisms, m. p. 110°, and thin needles, m. p. 175° (modifications "*a*" and "*β*"); bromoanisaldehyde forms *benzoyl-3-bromo-4-methoxyphenylethylene oxide*, very long needles, m. p. 158°; nitroanisaldehyde yields *benzoyl-3-nitro-4-methoxyphenyl-ethylene oxide*, short prisms, m. p. 172—173°; bromopiperon-aldehyde gives *benzoyl-(?)-bromo-3:4-methylenedioxyphenylethylene oxide*, needles, m. p. 98—98·5°; *m*-nitrocinnamaldehyde produces *benzoyl-m-nitrostyrylethylene oxide*.

$$COPh·CH{\overset{CH·CH:CH·C_6H_4·NO_2}{\underset{O}{<}}}$$
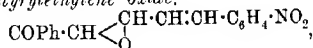
yellow crystals, m. p. 115—116°; terephthalaldehyde forms *benzoyl-p-aldehydophenylethylene oxide*, m. p. 116—119°.

Under the same conditions, benzoylacetone forms *a-acetyl-aβ-dibenzoylethane* (*acetyldiphenacyl*) in colourless cubes, m. p. 88—89°, which may be hydrolysed to diphenacyl, thus:

$$CHAc:CPh·ONa + COPh·CH_2Br \longrightarrow CHAcBz·CH_2Bz \overset{NaOH}{\longrightarrow}$$

$$CH_2Bz·CH_2Bz + Ac·ONa.$$
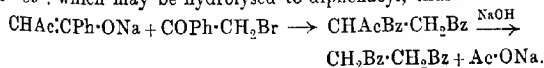
p-Chloroacetylanisole   (ω-chloro-*p*-methoxyacetophenone)   and anisaldehyde react to form *anisoylanisylethylene oxide*,

$$OMe \cdot C_6H_4 \cdot CO \cdot CH {\overset{CH \cdot C_6H_4 \cdot OMe}{\underset{O}{\big<}}}$$
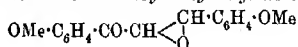
glistening, rhombic scales, m. p. 118—119°.

As has been mentioned already (*loc. cit.*), these ethylene oxides may be condensed with a further proportion of ω-bromoaceto-phenone to form dioxides. Thus, benzaldehyde may be converted into *α-benzoyl-βδ-diphenylbutadiene dioxide* (I), which crystallises in long needles, m. p. 156°. When boiled with aqueous-alcoholic potassium hydroxide, this dioxide yields *αγδ-trihydroxy-αβδ-tri-phenyl*-n-*valeric acid* (II), m. p. 178—179°, which forms a *tri-benzoate*, m. p. 150—150·5°. The reaction apparently follows the course indicated, thus:

$$COPh \cdot CH \overset{}{\underset{\diagdown \diagup}{}} CPh \cdot CH \overset{}{\underset{\diagdown \diagup}{}} CHPh \rightarrow COPh \cdot CO \cdot CHPh \cdot CH {\overset{CHPh}{\underset{O}{\big<}}}$$

$$\overset{}{\underset{O \qquad O}{}}$$

(I.)

$$CO_2H \cdot CPh(OH) \cdot CHPh \cdot CH {\overset{CHPh}{\underset{O}{\big<}}}$$

$$CO_2H \cdot CPh(OH) \cdot CHPh \cdot CH(OH) \cdot CHPh \cdot OH$$
$$\text{(II.)}$$
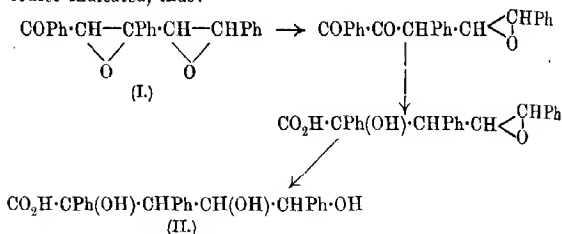
A different type of dioxide is obtained by condensing a dialdehyde with a bimolecular quantity of ω-bromoacetophenone. Thus, terephthalaldehyde gives *phenylenebisdibenzoylethylene oxide*,

$$COPh \cdot CH \overset{}{\underset{\diagdown \diagup}{}} CH \cdot C_6H_4 \cdot CH \overset{}{\underset{\diagdown \diagup}{}} CH \cdot COPh$$
$$\overset{}{\underset{O \qquad\qquad O}{}}$$
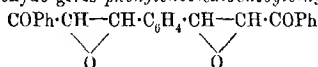
which crystallises in thin, pearly scales, m. p. 220—222°, and may be reduced by potassium iodide in glacial acetic acid to tere-phthalylidenediacetophenone, $C_6H_4(CH:CH \cdot COPh)_2$, the product being identical with that obtained by the condensation of aceto-phenone with telephthalaldehyde (see Lendenfeld, A., 1907, i, 221).

Benzoyl-*m*-nitrophenylethylene oxide reacts with stannic chloride as though it were a diketone, but the *product*, $C_{15}H_{11}O_4N,SnCl_4$, crystallising in large, yellowish-brown groups, is not identical with that given by the genuine diketonic isomeride,

$$COPh \cdot CO \cdot CH_2 \cdot C_6H_4 \cdot NO_2.$$
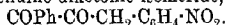
Widman has shown that benzoylphenylethylene oxide reacts with hydroxylamine under different conditions to form various com-pounds, partly oximes and partly cyclic substances (A., 1917, i, 221). Benzoyl-*m*-nitrophenylethylene oxide gives equally com-plicated reactions. When boiled with hydroxylamine hydrochloride and alcohol, it yields 3-*phenyl*-5-m-*nitrophenylisooxazole*,

$$N {\overset{CPh \cdot CH}{\underset{O——C \cdot C_6H_4 \cdot NO_2}{\big<}}},$$
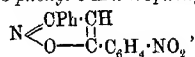
in thin tablets, m. p. 176—177°, which may also be prepared in the same way from the isomeric phenyl *m*-nitro-α-hydroxystyryl ketone (*loc. cit.*, 224). The mother liquor from this contains an *oxime*, "α," m. p. 121·5°, which is soluble in sodium hydroxide and non-reducible by hydriodic acid, and gives an *acetate*, large flakes, m. p. 132—132·5°. If the ethylene oxide is boiled with hydroxylamine hydrochloride and sodium acetate in alcohol, it yields another *oxime*, "β," which crystallises in slender needles, m. p. 145°, forms an *acetate*, prisms, m. p. 123°, changes into the α-oxime when treated with hydrochloric acid, and into a third *oxime*, "γ," small, glassy cubes, m. p. 153°, when crystallised from methyl alcohol, and produces 4- or 5-*hydroxy-3-phenyl*-5-m-*nitrophenyl*iso-*oxazolidine*,

$$NH<{CHPh \cdot CH \cdot OH \atop O----CH \cdot C_6H_4 \cdot NO_2} \quad or \quad NH<{CHPh \cdot CH_2 \atop O----C(OH) \cdot C_6H_4 \cdot NO_2},$$
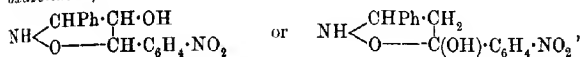
prisms, m. p. 145—146° (*nitroso*-compound, m. p. 135—140°), when boiled with potassium iodide and glacial acetic acid.

Benzoyl-*m*-nitrophenylethylene oxide reacts with semicarbazide acetate in cold alcohol to form 4-*hydroxy-3-phenyl*-5-m-*nitrophenyl*-4:5-*dihydropyrazole*-1-*carboxylamide*,

$$NH_2 \cdot CO \cdot N<{CH(C_6H_4 \cdot NO_2) \cdot CH \cdot OH \atop N======CPh},$$
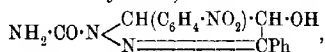
which crystallises in short prisms, m. p. 162—163° (decomp.). The same compound is given by the corresponding chlorohydrin, $OH \cdot CHBz \cdot CHCl \cdot C_6H_4 \cdot NO_2$, but the isomeric phenyl *m*-nitro-α-hydroxystyryl ketone yields a different product, namely, the normal *semicarbazone*, $NH_2 \cdot CO \cdot NH \cdot N \colon CPh \cdot CH \colon C(OH) \cdot C_6H_4 \cdot NO_2$, m. p. 120–125° (decomp.). Similarly, the chlorohydrin usually reacts with hydrazine hydrate to form 4-*hydroxy-3-phenyl*-5-m-*nitro-phenyl*-4:5-*dihydropyrazole*, in rhombic leaflets, m. p. 184—185°, but on one occasion 4-*hydroxy*-5-*hydrazino*-3-*phenyl*-5 m-*nitro-phenyl*-4:5-*dihydropyrazole* was obtained instead, in yellow needles, m. p. 165°.

Thiocyanic acid and thiocarbamides also condense with benzoyl-*m*-nitrophenylethylene oxide, water being eliminated. Thiocyanic acid gives a *compound* which crystallises in pale yellow prisms, m. p. 120—125° (decomp.), forms an *acetyl* derivative, m. p. 111°, and is probably represented by the formula

$$CO<{NH \cdot CHBz \atop S----CH \cdot C_6H_4 \cdot NO_2}.$$
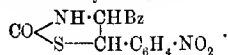
Thiocarbamide gives a deep yellow *product*, m. p. 176–177° (decomp.), to which the alternative formulæ,

$$NH \colon C<{NH \cdot CHBz \atop S----CH \cdot C_6H_4 \cdot NO_2} \quad or \quad NH \colon C<{NH \cdot CH \cdot C_6H_4 \cdot NO_2 \atop S----CHBz},$$
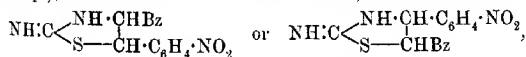
are assigned. Thiocarbanilide forms a yellow *product*, m. p. 221° (decomp.), which would be the diphenyl derivative of the foregoing substance. It gives unstable additive compounds with bromine

and iodine, and is converted by boiling with sodium ethoxide solution into an orange-red *isomeride*, m. p. 245°.   J. C. W.

Action of Light on Keto-oxido-compounds. SVEN BODFORSS (*Ber.*, 1918, **51**, 214—219).—Benzoylphenylethylene oxide, benzoyl-*m*-nitrophenylethylene oxide, and benzoyl-*p*-chlorophenylethylene oxide undergo rearrangement into phenyl α-hydroxystyryl ketones with increasing readiness when their methyl-alcoholic solutions are exposed to the light of a mercury lamp. The yields of the isomerides are very small, but their presence can be demonstrated by the ferric chloride test for enols and by the precipitation of copper salts, from which they can eventually be isolated.

The production of phenyl *m*-nitro-α-hydroxystyryl ketone by another method has already been described (A., 1917, i, 224). A third method consists in the action of *m*-nitrobenzoyl chloride on benzoylacetone in the presence of sodium ethoxide, followed by hydrolysis of the acetyl derivative by boiling hydrochloric acid. *Phenyl p-chloro-α-hydroxystyryl ketone*, $COPh \cdot CH \colon C(OH) \cdot C_6H_4Cl$, very pale yellow crystals, m. p. 89°, is also prepared as follows: *p*-chlorobenzylideneacetophenone is treated with bromine, when two isomeric *dibromides*, $COPh \cdot CHBr \cdot CHBr \cdot C_6H_4Cl$, are formed, a sparingly soluble one, m. p. 178—180°, decomp. 190—193°, and a freely soluble one, m. p. 125—126°, decomp. 142—143°, either of which gives the desired keto-enol on boiling with alcoholic potassium hydroxide.   J. C. W.

Action of Hydriodic Acid on Cinchonine and its Isomerides. Cinchoniline, Cinchonigine, and *apo*Cinchonine. E. LÉGER (*Compt. rend.*, 1918, **166**, 469—472. Compare this vol., i, 121).—When heated with hydriodic acid, cinchonine and cinchoniline give the same hydriodocinchonine, whilst cinchonigine and *apo*cinchonine give an isomeric *hydriodo*apo*cinchonine*, as shown by a study of the optical activity of the dihydrochlorides and dinitrates of the four hydriodo-derivatives.   W. G.

Preparation of Histidine. HARRY M. JONES (*J. Biol. Chem.*, 1918, **33**, 429—431).—Two litres of hydrochloric acid are added to an equal volume of the concentrated suspension of red blood corpuscles obtained by centrifugalising defibrinated ox blood. The mixture is boiled on a sand-bath for eighteen hours, or until the biuret reaction is negative. After exactly neutralising by the addition of about an equal volume of saturated sodium carbonate solution, the mixture is filtered, and ammonia removed from the filtrate by boiling for an hour with 25 grams or more of sodium hydroxide. On cooling, leucine and tyrosine are deposited, and should be filtered off. The histidine is now precipitated by the alternate addition of concentrated solutions of mercuric chloride and sodium carbonate until a filtered portion no longer gives a voluminous precipitate with the mercuric chloride solution. The precipitate is collected, washed, suspended in five times its volume

of water, and, using hydrochloric acid, the latter rendered acid to bromophenol-blue ($p_H=3$). The mercury–histidine compound dissolves, and, after filtration, is reprecipitated by sodium carbonate. It is finally suspended in water and the histidine liberated by hydrogen sulphide. After filtration, the filtrate is concentrated at the ordinary temperature, whereon large, yellow crystals of histidine hydrochloride separate from the brown, syrupy mother liquor. The yield is about 15 grams.   H. W. B.

Conversion of Cocaine into New, Physiologically Active Substances. J. VON BRAUN and E. MÜLLER (*Ber.*, 1918, **51**, 235—252).—Von Braun has begun an inquiry into the interesting question of the influence on physiological activity of displacing some specific group or other from one position to another in the molecule of an active drug. So far, he has experimented on codeine (A., 1916, i, 665; 1917, i, 163), but this is not quite a suitable material, as its constitution is still not definitely known. The problem has now been attacked in the group of the tropeines, in which the presence of an acylated hydroxyl group in the γ-position with regard to the basic nitrogen atom may be regarded as the factor controlling the physiological behaviour. The question raised, therefore, in this paper is what is the effect of displacing the hydroxyl group to another part of the molecule, still in the γ-position with regard to the nitrogen atom? Cocaine (I) has been converted into two such compounds, II and III.

$$CH_2 \cdot CH—CH \cdot CO_2Me$$
$$|\quad NMe \quad CH \cdot OBz$$
$$CH_2 \cdot CH—CH_2$$
(I.)

$$CH_2 \cdot CH—CH \cdot CH_2 \cdot O \cdot CO \qquad CH_2 \cdot CH——CH \cdot CO_2Et$$
$$|\quad NMe \quad CH_2 \qquad CHPh \qquad |\quad N———|—CH_2 \cdot CH_2 \cdot CH_2 \cdot OBz$$
$$CH_2 \cdot CH—CH_2 \qquad CH_2 \cdot OH \qquad CH_2 \cdot CH—CH_2 \cdot CH_2$$
(II.) \qquad\qquad\qquad (III.)
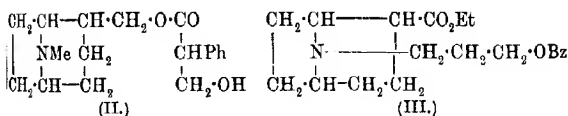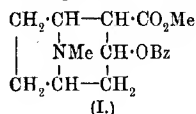
Compound II is actually found to be as effective a mydriatic as atropine, and III as powerful a local anæsthetic as cocaine. It follows, therefore, that it does not matter where the acyloxy-group is with regard to the tropane ring as long as it is in the γ-position with respect to the nitrogen atom.

Cocaine is converted by well-known methods into ecgonidine (formerly anhydroecgonine), and this into the ethyl ester (annexed formula). This is reduced by means of

$$CH_2 \cdot CH—CH \cdot CO_2Et$$
$$|\quad NMe \quad CH$$
$$CH_2 \cdot CH—CH$$

hydrogen and palladium to *ethyl dihydroecgonidine*, b. p. 127—129°/12 mm., which forms an *aurichloride*, yellow leaflets, m. p. 167°, and a *methiodide*, long needles, m. p. 219°. Willstätter (A., 1897, i, 385) reduced the ester by means of sodium and amyl alcohol; his pro-

duct had the same b. p., but gave quite different salts, and it is
fairly obvious that transformation about the asymmetric carbon
atom had occurred to a considerable extent in his experiment. The
next stage consists in reducing the ester by means of sodium and
alcohol to the hydramine, and Willstätter's product gives the same
result as the above.   The new base, *homotropine* (annexed
formula), crystallises in needles, m. p.
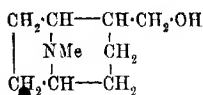
$$CH_2 \cdot CH \!-\!\!\!- CH \cdot CH_2 \cdot OH$$
$$| \quad\quad\quad\quad |$$
$$NMe \quad CH_2$$
$$| \quad\quad\quad\quad |$$
$$CH_2 \cdot CH \!-\!\!\!- CH_2$$

85°, $[\alpha]_D^{20} + 22 \cdot 48°$ (in alcohol), and
forms a *hydrochloride*, m. p. 192°, an
aurichloride, m. p. 191°, a *picrate*, thin
needles, m. p. 208—209°, and a *methiodide*, which may be converted into a

platinichloride, m. p. 183°, and an *aurichloride*, yellow leaflets,
m. p. 238°. The *benzoate* is produced by means of benzoyl
chloride; it is a viscous oil, which forms a *platinichloride*, m. p.
201°, an *aurichloride*, m. p. 161°, and a lemon-yellow *picrate*, m. p.
177°. *Homotropine tropate* (II) is prepared by warming the
hydrochloride with acetyltropyl chloride, hydrolysing the product
by warm water to remove the acetyl group, and adding dilute
sodium hydroxide to the solution; it is obtained as an oil, which
forms a *platinichloride*, m. p. 192°. The oily *mandelate* and its
platinichloride, m. p. 192°. are formed in the same way.

For the preparation of the other compound (III), cocaine is first
treated with cyanogen bromide in warm chloroform, when *cyano-
norcocaine* (IV), m. p. 123—124°, is produced. This is heated

$$CH_2 \cdot CH \!-\!\!\!- CH \cdot CO_2Me \quad\quad CH_2 \cdot CH \!-\! CH \cdot CO_2Et$$
$$| \quad\quad\quad\quad | \quad\quad\quad\quad\quad\quad | \quad\quad\quad |$$
$$N \cdot CN \quad CH \cdot OBz \quad\quad\quad\quad NH \quad CH$$
$$| \quad\quad\quad\quad | \quad\quad\quad\quad\quad\quad | \quad\quad\quad ||$$
$$CH_2 \cdot CH \!-\!\!\!- CH_2 \quad\quad\quad\quad CH_2 \cdot CH \!-\! CH$$
$$\text{(IV.)} \quad\quad\quad\quad\quad\quad\quad \text{(V.)}$$
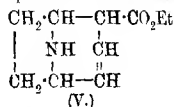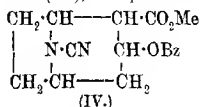
with concentrated hydrochloric acid at 120°, and thus converted
directly into *norecgonidine*, which is very sparingly soluble in
alcohol, has m. p. 254—255°, forms a *hydrochloride*, m. p. 257°, a
platinichloride. m. p. 251°, an *aurichloride*, m. p. 204°, and an
ethyl ester (V), a basic-smelling oil, b. p. 157°/25 mm., which gives
a very hygroscopic *hydrochloride*, long needles, an *aurichloride*,
m. p. 133°, and a *benzoyl* derivative. m. p. 114°. Norecgonidine
may also be prepared by first treating ethyl ecgonidine (above)
with cyanogen bromide, but the yield is very small, rupture of the
tropane ring being the main result.   The ester V is hydrogenated
in the presence of palladium, giving *ethyl dihydronorecgonidine*,
b. p. 135—137°/19 mm., D_4^{19} 1·0856, $[\alpha]_D^{19} + 5 \cdot 881°$, which yields a
hygroscopic *hydrochloride*, m. p. 149—150°, and an *aurichloride*,
m. p. 110°. The N-γ-*benzoyloxypropyl* derivative (III) is pre-
pared by the action of γ-bromopropyl benzoate (compare A., 1916,
i, 631); it is an oil which forms a *hydrochloride*, long needles, m. p.
142°, a *platinichloride*, m. p. 94—95°, and an *aurichloride*, m. p.
127—128°.

Another interesting product is obtained by the action of γ-bromo-
propyl benzoate on the ester V. It is designated *eccaine*, and is

an oil which forms a *hydrochloride*, m. p. 117°, a *picrate*, m. p. 139—141°, and a *methiodide*, m. p. 194—195°. It is more active as an anæsthetic than cocaine, is non-toxic, and so stable that its solutions may be sterilised easily. J. C. W.

Preparation of Homotropine. CHEMISCHE WERKE, GRENZACH (D.R.-P., 296742; from *Chem. Zentr.*, 1917, i, 612).—Compare preceding abstract. J. C. W.

Preparation of *N*-Demethylated Derivatives of the Alkaloids of the Cocaine and Atropine Groups, their Derivatives and Salts. CHEMISCHE WERKE, GRENZACH (D.R.-P., 301870; from *Chem. Zentr.*, 1918, i, 250).—Compare von Braun and Müller (above). Acetyltropine reacts with cyanogen bromide to give *acetylcyanonortropine*, m. p. 96°, which yields nortropine on boiling with moderately concentrated hydrochloric acid. J. C. W.

Production of Derivatives of Homotropine. CHEMISCHE WERKE, GRENZACH (D.R.-P., 299806; from *Chem. Zentr.*, 1917, i, 510).—The pharmacologically inactive homotropine can be rendered active by esterification with organic acids such as benzoic, tropic, or mandelic acid, the resulting esters (see von Braun and Müller, preceding page) resembling atropine in their effect on the animal organism. In this way, anhydroecgonine, hitherto value-less, can be converted into therapeutically useful products. D. F. T.

New Cases of Isomerism in the Isatin Series. GUSTAV HELLER [with FRITZ BAUMGARTEN] (*Ber.*, 1918, 51, 180—190. Compare A., 1917, i, 219).—The discovery of three different forms of isatin, or at least ethers of three forms, has led the author to examine 5:7-dimethylisatin, with the surprising and so far in-explicable result that no fewer than four individual isomerides have been obtained. These are numbered I, II, III, and IV, for the time being, in the order of their discovery.

Isomeride I.—This is the normal product, $C_6H_2Me_2{<}{CO \atop NH}{>}CO$, obtained originally from dichloroacetic acid and 1:3:4-xylidine (A., 1908, i, 218). It crystallises in yellow needles, m. p. 243°, and forms a greyish-red N-*silver* salt, from which 1:5:7-*trimethylisatin* may be obtained, in dark red leaflets, m. p. 214°, this yielding a yellow *phenylhydrazone*, m. p. 161°. The sodium salt of the isatin reacts with silver nitrate to form a very dark brown O-*silver* salt, $C_6H_2Me_2{<}{CO \atop N}{>}C·OAg$, but this yields the original isatin on acidification or treatment with methyl iodide, and not the lactim modification or its methyl ether.

Isomeride II.—This is produced by the action of benzoyl chloride on the above *N*-silver salt, suspended in warm benzene. It crystallises in large, dark red, oblique prisms, m. p. 204° (decomp.); it gives the indophenin reaction at once, whereas the colour only develops slowly with isomeride I; it dissolves in pure sulphuric acid with dark violet colour, whereas isomeride I gives a ruby-red solution; it is insoluble in sodium hydroxide solution; it forms a *phenylhydrazone*, which is fairly soluble in alcohol and crystallises in yellow needles, m. p. 216° (decomp.), whereas the phenylhydrazone of isomeride I is very sparingly soluble and has m. p. 272°; and it reacts with methyl sulphate, which isomeride I does not, giving a *methyl ether*, quadratic, red tablets, m. p. 247° (decomp.), which forms a yellowish-red *phenylhydrazone*, m. p. 203°. These reactions serve to establish the fact that the second isomeride is a distinct individual, but that it is neither the lactim modification nor the expected isatol, that is, neither

$$C_6H_2Me_2\!\!<\!\!^{CO}_{-N}\!\!>\!\!C\cdot OH \quad nor \quad C_6H_2Me_2\!\!<\!\!^{C(OH)}_{N\underline{}}\!\!>\!\!CO.$$
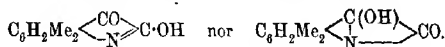
Isomeride III.—This is formed by triturating isomeride II with dilute sodium hydroxide, when a red, sparingly soluble sodium salt is produced, which is acidified. It crystallises in bluish-red, rectangular prisms, m. p. 279°; it yields the same sodium salt when mixed with sodium hydroxide, but if the suspension is kept, the colour fades and the isomeride I may be recovered on acidifying; it is freely soluble in dilute sodium carbonate or ammonia; it does not give the indophenin reaction, and its solution in concentrated sulphuric acid is only faintly reddish-yellow; it does not give a phenylhydrazone; it forms a bluish-red *silver* salt; and it may be converted, through the sodium or silver salts, or by means of diazomethane, into a *methyl ether*, yellowish-red tablets, m. p. 210°, insoluble in warm, dilute alkali hydroxides. This modification therefore conforms to the type of isatol.

Isomeride IV.—This is produced when isomeride III is crystallised from hot acetic acid. It has m. p. 267°, forms a readily hydrolysable, colourless sulphate, dissolves in alcoholic potassium hydroxide, does not yield a phenylhydrazone, and reacts with diazomethane to form a *methyl ether*, fiery-red, glistening, flat prisms, m. p. 211°, which depresses the m. p. of the methyl derivative of isomeride III. The compound is therefore another isatol.

There are, apparently, two pairs of structurally similar isomerides, I and II being of the normal isatin type and III and IV of the isatol series, but I and III resemble each other in their acidic properties and II and IV in their neutral or basic properties.

J. C. W.

Bz-**Hydroxyindolinones [Hydroxyoxindoles].** GEORG WAHL (*Monatsh.*, 1918, **38**, 525—535).—No oxindole has hitherto been prepared containing a hydroxyl group in the benzene nucleus. By extending the indolinone synthesis, based on the

elimination of ammonia from aliphatic phenylhydrazides (Brunner, A., 1897, i, 100), to the corresponding anisylhydrazides, it is possible to obtain 5-methoxyoxindole derivatives. Thus, iso*butyryl p-anisylhydrazide*, colourless leaflets or granules, m. p. 142°, when heated with lime at approximately 180° for about two hours, yields *5-methoxy-3:3-dimethyloxindole*, $\begin{matrix} CMe_2-CO \\ C_6H_3(OMe) \end{matrix}\!\!>NH$, rhombic tablets, m. p. 150° (*bromo*-derivative $C_{11}H_{12}O_2NBr$, colourless needles, m. p. 218°; *acetyl* derivative, needles, m. p. 84°; *benzoyl* derivative, needles, m. p. 82°; *silver* salt, very unstable, greenish-white, gelatinous mass), accompanied by a little *iso*butyrylamide, leaflets, m. p. 124°. By treating with boiling hydriodic acid for one hour, the methoxyl compound is converted into *5-hydroxy-3:3-dimethyloxindole*, $\begin{matrix} CMe_2-CO \\ C_6H_3(OH) \end{matrix}\!\!>NH$, colourless needles, m. p. 244°; *diacetyl* derivative, colourless needles, m. p. 126°; *benzoyl* derivative, $C_{17}H_{15}O_3N$, needles, m. p. 240°. In a similar manner, iso*butyryl o-anisylhydrazide*, m. p. 120°, when heated with lime, is converted into *7-methoxy-3:3-dimethyloxindole*, $C_{11}H_{13}O_2N$, colourless needles, m. p. 101° (*bromo*-derivative, $C_{11}H_{12}O_2NBr$, colourless needles, m. p. 200°), which is demethylated by hydriodic acid with formation of *7-hydroxy-3:3-dimethyloxindole*, $C_{10}H_{11}O_2N$, m. p. 250°. D. F. T.

Selenomethylene-blue. P. KARRER (*Ber.*, 1918, **51**, 190—192). —In his account of some new selenazine dyes, the author showed that the true selenium analogue of methylene-blue had not yet been described, references to such a dye being erroneous (A., 1916, i, 434). The compound is easily prepared by Kehrmann's method (*ibid.*, 435). Selenodiphenylamine is treated with bromine in glacial acetic acid until phenazselenonium perbromide is completely precipitated, in brightly shimmering, brown flakes, and this is triturated with an alcoholic solution of dimethylamine. *3:6-Tetramethyldiaminophenazselenonium bromide* (*selenomethylene-blue bromide*), $NMe_2 \cdot C_6H_3 \ll\!\!\begin{matrix} N \\ SeBr \end{matrix}\!\!> C_6H_3 \cdot NMe_2$, is formed, and, after crystallisation from boiling water, is obtained in shimmering needles with metallic green reflex, possessing the same stability and tinctorial properties as methylene-blue. J. C. W.

Action of Aniline on Carbon Tetrachloride. ERNST JOHANNES HARTUNG (T., 1918, **113**, 163—168).—In 1858, Hofmann showed that carbon tetrachloride and aniline react at 180° to form pararosaniline and diphenylaminobenzamidine,

$$NHPh \cdot C(NPh) \cdot C_6H_4 \cdot NH_2.$$
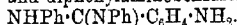
This reaction has now been studied at lower temperatures and in the presence of a copper–mercury couple as a catalyst.

The two liquids react even at the ordinary temperature. Brown discolorations soon appear, but the first definite product, after

some weeks' action, seems to be *s*-diphenylcarbamide. The production of this can be traced to the action of moisture on a dichloro-compound, $CCl_2(NHPh)_2$. After some months, diphenylaminobenzamidine separates. The by-products vary according to the proportions of the reagents employed. With a very large excess of carbon tetrachloride, a compound which crystallises in small, reddish-brown prisms, m. p. 245° (corr.), and a dark blue dye separate, as well as diphenylcarbamide, during the early months.

In the presence of amalgamated copper, the mixtures solidify within a few days, diphenylaminobenzamidine hydrochloride being the chief product, accompanied by azobenzene, phenylcarbylamine, and a little pararosaniline. The reaction is still more rapid at 80—90°, but is never complete, and many obscure by-products are formed.

Diphenylaminobenzamidine hydrochloride becomes yellow on rubbing, but reverts to white after some days. These changes can be induced repeatedly. J. C. W.

Reactions of the Formamidines. VII. The Constitution of some Pyrazole Derivatives. F. B. DAINS and ROLLA N. HARGER (*J. Amer. Chem. Soc.*, 1918, **40**, 562—569. Compare A., 1902, i, 602; 1906, i, 781; 1913, i, 1086, 1096; 1916, i, 676).—It has already been shown that the substituted formamidines react with compounds containing methylene hydrogen, giving rise to products in which the –CH₂– group is replaced by the grouping :CH·NHR. By the action of hydrazine on amino-methylene derivatives of ethyl acetoacetate, it is now found that derivatives of 5-methylpyrazole-4-carboxylic acid can be obtained.

m-Bromoanilinomethyleneacetoacetanilide,
$$NHPh·CO·CAc:CH·NH·C_6H_4Br,$$
yellowish-white needles, m. p. 113°, prepared by the interaction of *m*-dibromodiphenylformamidine and acetoacetanilide or aceto-*p*-toluidide, reacts with hydrazine in alcoholic solution, yielding *5-methylpyrazole-4-carboxyanilide*,
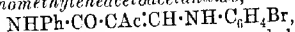
$$\begin{matrix} N{=\!=}CH \\ NH·CMe \end{matrix}{\Large >}C·CO·NHPh,$$
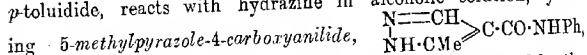
needles, m. p. 179°, the same substance also being obtained by the action of hydrazine on anilinomethyleneaceto-*p*-toluidide, the reaction product of acetoaceto-*p*-toluidide and diphenylformamidine. When heated together at 120—130°, ethyl acetoacetate and *o*-phenetidine undergo condensation, with formation of *acetoaceto-o-phenetidide*, $CH_2Ac·CO·NH·C_6H_4·OEt$, needles, m. p. 92°, which is capable of reacting with diphenylformamidine, with formation of *anilinomethyleneacetoaceto-o-phenetidide*,
$$NHPh·CH:CAc·CO·NH·C_6H_4·OEt,$$
needles, m. p. 135°; hydrazine or hydrazine hydrate converts this into *5-methylpyrazole-4-carboxy-o-phenetidide*,
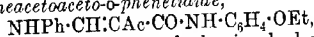
$$\begin{matrix} N{=\!=}CH \\ NH·CMe \end{matrix}{\Large >}C·CO·NH·C_6H_4·OEt,$$
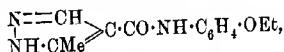
needles, m. p. 163°; *hydrochloride*, m. p. 200° (decomp.). At

100°, ethyl acetoacetate reacts with di-*o*-phenetidylformamidine, giving *ethyl o-phenetidinomethyleneacetoacetate*, $C_{15}H_{19}O_4N$, colourless crystals, m. p. 111°, which on treatment in hot alcoholic solution with hydrazine hydrate yields *ethyl 5-methylpyrazole-4-carboxylate*, $\underset{NH \cdot CMe}{\overset{N=CH}{\Big\rangle}} C \cdot CO_2Et$, needles with $1H_2O$, m. p. 46°, or m. p. 54° when anhydrous.

Phenylhydrazine reacts with anilinomethyleneacetylacetone, giving rise to 4-acetyl-1-phenyl-5-methylpyrazole, in agreement with Claisen's results (A., 1897, i, 441), but with ψ-cumidinomethyleneacetylacetone and *p*-toluidinomethyleneacetylacetone, this product is accompanied by the *phenylhydrazone*, yellow needles, m. p. 175°, of the acetylphenylmethylpyrazole. The reaction product of acetylphenylmethylpyrazole and hydrazine hydrate in alcoholic solution is the corresponding *hydrazone*, $\underset{NPh \cdot CMe}{\overset{N=CH}{\Big\rangle}} C \cdot CMe \colon N \cdot NH_2$, four-sided prisms, m. p. 94·5° (*hydrochloride*, m. p. 218°; *benzylidene* derivative, $C_{10}H_9N_2 \cdot CMe \colon N \cdot N \colon CHPh$, yellow crystals, m. p. 127°), which when warmed with a little formic or acetic acid in ethyl acetate solution undergoes intermolecular condensation, with formation of hydrazine and *bis-4-acetyl-1-phenyl-5-methylpyrazolylazine*, $N_2(\colon CMe \cdot C_{10}H_9N_2)_2$, yellow crystals, m. p. 174°; this, on boiling with hydrochloric acid, regenerates the original pyrazole compound. When *o*-phenetidinomethyleneacetylacetone and hydrazine hydrate are warmed together in alcoholic solution, a yellow compound, m. p. 320°, is obtained; this has already been described by Gaugler and by J. Gattermann (*Diss.*, Freiburg, 1903 and 1904), who regarded it as the triazine, $\underset{CH_2 \cdot C \colon N-NH}{\overset{CH=C \cdot CMe \colon N}{|\qquad\quad|}}$, but a more probable constitution is that of the azine derivative of 4-acetyl-5-methylpyrazole.

During the course of the investigation, *acetoaceto-m-bromoanilide*, $CH_3Ac \cdot CO \cdot NH \cdot C_6H_4Br$, plates, m. p. 83°, and *m-bromoanilinomethyleneacetoaceto-m-bromoanilide*,

$$C_6H_4Br \cdot NH \cdot CO \cdot CAc \colon CH \cdot NH \cdot C_6H_4Br,$$
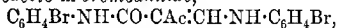
pale yellow needles, m. p. 154°, were prepared, the latter by the interaction of ethyl acetoacetate and di-*m*-bromodiphenylformamidine. It was also found that the benzoyl derivative of *m*-bromoaniline has m. p. 135—136° instead of 120°, as stated earlier (Kottenhahn, A., 1891, 1237). The results of the investigation demonstrate that the reaction products of hydrazine or phenylhydrazine and arylaminomethyleneacetoacetoarylamides are pyrazole compounds, and not pyrazolone derivatives, as has been assumed earlier (Ruggeburg, *Diss.*, Freiburg, 1903; J. Gattermann, *Diss.*, 1904). D. F. T.

Preparation of Mono-azo-dyes suitable for the Manufacture of Pigments. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P., 297414; from *Chem. Zentr.*, 1917, i, 981—982).—In place of 1-benzoylamino-7-hydroxynaphthalene, or derivatives of

this containing substituents in the benzoyl radicle, the correspond-
ing *N*-alkyl compounds can be used. 1-Benzoylethylamino-7-
hydroxynaphthalene, 1-benzoylmethylamino-7-hydroxynaphthalene,
and   1 : 2′-chlorobenzoylethylamino-7-hydroxynaphthalene   have
m. p. 224—225°, 186—187°, and 232—233° respectively.

D. F. T.

**Structure of Yeast-nucleic Acid. III. Ammonia Hydro-
lysis.** P. A. LEVENE (*J. Biol. Chem.*, 1918, **33**, 425—428. Compare
this vol., i, 130).—Uridinephosphoric acid can be isolated from
the products of the hydrolysis of yeast-nucleic acid by dilute
ammonia at 115° through the intermediate formation of the mixed
brucine salts of the cytosine and uracil nucleotides, which, after
separation, are converted into the barium salts, as previously
described (*loc. cit.*).   H. W. B.

**Effects of Electrolytes on Gelatin and their Biological
Significance. II. Effect of Salts on the Precipitation of
Acid and Alkali-gelatin by Alcohol. Antagonism.** W. O.
FENN (*J. Biol. Chem.*, 1918, **33**, 439—451. Compare this vol.,
i, 198).—Employing the technique previously described, the author
finds that the effect of combinations of salts with acids and alkalis
on the precipitability of the gelatin by alcohol is greater or less
than the effect produced by the acid or alkali alone, according to
the valency of the ions in the salt. Thus, salts with univalent
ions (like sodium chloride) decrease the effect of both acids and
alkalis on the precipitability of gelatin. Salts with bivalent or
tervalent ions (like calcium or aluminium chloride) decrease the
effect of alkalis on gelatin, but increase the effect of acid, except
in high concentrations of salt or acid, where the effect is decreased.
Salts with bivalent or tervalent anions (like sodium sulphate or
citrate) decrease the effect of acids on gelatin, but increase the
effect of alkalis, except at high concentration, when the greater the
concentration of either salt or alkali, the less the alcohol necessary
for precipitation. These results are comparable and in some
respects analogous to the antagonistic effects of various electrolytes
observed in certain biological phenomena (compare Loeb, A., 1916,
i, 186, and this vol., i, 51).   H. W. B.

Ionisation of Proteins and Antagonistic Salt Action.
JACQUES LOEB (*J. Biol. Chem.*, 1918, **33**, 531—549. Compare A.,
1917, ii, 453, and Fenn, preceding abstract).—The author describes
a new method of studying the effect of neutral salts on gelatin in
which the powdered protein is treated with the salt in a concen-
tration of $M/4$ or $M/8$, and then the excess of salt is removed by
washing with water or with a weak solution of another salt. In
these circumstances, the initial swelling occurring in $M/8$-sodium
chloride is greatly increased by perfusion with water or a weak
solution of a neutral salt with a univalent metal. The additional
swelling is only possible as long as the weaker solution remains
below a certain concentration, and it is found that the limiting

molecular concentration which will cause the additional swelling is twice as great if the anion is univalent as when it is bivalent, regardless of the nature of the anion and cation. The influence of neutral salts on the swelling of gelatin is therefore of a stoicheiometric order, and the inhibiting action of a salt on the additional swelling is explained by the author as being due to a diminution of the degree of electrolytic dissociation of a metal–protein compound first produced. Thus, neutral salts with a univalent cation like sodium chloride in concentrations of $M/8$ or $M/4$ form highly ionisable salts with gelatin. On treatment with water, dissociation occurs into positively charged metal ions and negative gelatin ions, which may or may not contain the anion of the salt in non-dissociated bondage. It is the formation of these gelatin ions that causes the additional swelling observed. The metals of the alkaline earth group form salts with gelatin which are not capable of swelling and do not ionise. The transformation of gelatin salts with univalent cation (capable of swelling) into gelatin salts with bivalent cation (not capable of swelling) is the cause of the antagonistic action of the metals of the calcium group.

H. W. B

Physiological Chemistry.

The Presence of Hæmatin in Human Blood-serum. I. Joh. Feigl (*Biochem. Zeitsch.*, 1918, **85**, 171—187).—As a result, chiefly of clinical experience, hæmatin could be detected as a pathological constituent of the blood after intoxication by the following substances: chromates, chlorates, carbon monoxide, various gases, resorcinol, mono-, di-, and tri-nitrobenzene, picric acid, acetanilide, exalgin, p-phenylenediamine, pyrodine (acetylphenylhydrazine), maretine, trional, trigemine, excessive use of tobacco.

S. B. S.

The Presence of Hæmatin in Human Blood-serum. II. Joh. Feigl and Rud. Deussing (*Biochem. Zeitsch.*, 1918, **85**, 212—229).—This paper is chiefly of clinical interest, giving the results of the examination of the serum for the presence of hæmatin in about 700 cases.

S. B. S.

Chemical Studies on Physiology and Pathology. II. Immunity Reactions. G. Herzfeld and R. Klinger (*Biochem. Zeitsch.*, 1918, **85**, 1—44. Compare this vol., i, 47).—A theoretical paper, in which the authors develop further their conceptions of the nature of proteins, which have been already the subject of numerous papers. They conceive the antibodies as derived from the antigen itself; this undergoes a partial degradation in the body, and the degraded but still specific product is then adsorbed by certain protein particles of the blood (derived from the degrada-

tion of cells and in the "globulin" stage). The complex thus formed has the property of adsorbing new quantities of antigen, thus giving rise to the known immunity reactions, such as precipitation, deintoxication, etc. The ideas thus expressed are developed in considerable detail.   S. B. S.

Deaminisation and Carbamide Formation in the Animal Body. WILHELM LÖFFLER (*Biochem. Zeitsch.*, 1918, **85,** 230—294). —The surviving liver (rabbits and dogs) was perfused with Ringer's solution mixed with blood, and the ammonia and carbamide were estimated in the perfusing fluid both before and after perfusion. The carbamide was estimated by the urease method. It is shown that there is an increase in the carbamide after perfusion even when no nitrogen compound is added to the perfusion liquid. The addition of the ammonium salts of inorganic acids causes, however, a considerable addition to the amount of carbamide formed, leaving no doubt that the ammonium salts are converted into carbamide, and this happens even when the perfusing liquid is distinctly acid. Acids inhibit the formation of carbamide somewhat, without preventing it. Primary amines give rise to carbamide also when perfused through the liver, the lower amines, such as methylamine or ethylamine, being completely burnt, and the higher amines (amylamine, benzylamine, *p*-hydroxyaniline, and phenylethylamine) less completely. No substituted carbamides could be detected. Trimethylamine is completely demethylated in the liver, the ammonia being converted into carbamide.   S. B. S.

Presence of the Co-ferment of the Alcoholic Yeast Fermentation in Muscular Tissue and its Significance in the Respiratory Mechanism. OTTO MEYERHOF (*Zeitsch. physiol. Chem.*, 1918, **101,** 165—175).—The extracts of muscle and other tissues are prepared by boiling the minced tissue in an equal weight of water and filtering. Samples of yeast juice which have been inactivated by removal of the co-ferment by Harden and Young's method (A., 1907, i, 104) are reactivated by the addition of the tissue extract. The author finds that glycolysis by yeast or by muscle juice is similarly accelerated by the tissue extract (compare Harden and MacLean, A., 1911, ii, 215, 905).
                                                                 H. W. B.

The Synthesis of Luciferin. RAPHAEL DUBOIS (*Compt. rend.*, 1918, **166,** 578—580. Compare *ibid.*, 1917, **165,** 33, and Harvey, A., 1917, i, 365).--The author has extracted from *Pholade dactyle* a substance presenting all the characteristics of taurine, and also a luciferase which converts the taurine into luciferin.   W. G.

[Physiological] Action of an Isomeride of Caffeine. WILLIAM SALANT and HELENE CONNET (*J. Pharm. Exper. Ther.*, 1918, **11,** 81—88).—The authors find that 2:8-dioxy-1:7:9-trimethyl-1:2:8:9-tetrahydropurine (Johns, A., 1914, ii, 922) is

much less active physiologically than the isomeric 2:6-dioxy-compound (caffeine), the relative toxicity for rabbits of the two substances being about 1:11. The new isomeride caused a moderate increase in the secretion of urine in some experiments, but it failed to stimulate renal activity in others. When tested on frogs, it was found to act as a weak cardiac stimulant.   H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Disinfectant Action of Quinine Alkaloids on Pathogenic Bacteria. R. BIELING (*Biochem. Zeitsch.*, 1918, **85**, 188—211. Compare Schaeffer, this vol., i, 93).—The alkaloids investigated were quinine, optochine (ethylhydrocupreine), eucupine (*iso*amylhydrocupreine), and the *iso*octyl-, decyl-, and dodecyl-hydrocupreines. These have been found to have a specific disinfectant action on the bacilli of diphtheria. splenic fever. and tetanus. Eucupine and *iso*octylhydrocupreine are generally the most effective.   S. B. S.

Influence of Acids on Germination. L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1918, **166**, 547—552).—Mineral acids must be classed amongst those substances considered most injurious to germination. This toxic action may be modified by the presence of electrolytes in the form of salts, or by those that the acid may form by its action on the teguments of the seeds or the glass of the apparatus. Amongst these antitoxic substances, calcium appears to be one of the most powerful.   W. G.

The Assimilation of Carbon Dioxide. III. Behaviour of Colloidal Chlorophyll towards Carbon Dioxide. RICHARD WILLSTÄTTER and ARTHUR STOLL (*Ber.*, 1917, **50**, 1791—1801. Compare this vol., i, 207).—Solutions of chlorophyll in organic solvents do not absorb more carbon dioxide than the pure liquids, but the hydrosols absorb much more of the gas than other colloidal solutions, the absorption reaching a maximum of two molecular proportions to every magnesium atom. The absorption is attended by the precipitation of phæophytin, and the reaction may consequently be represented, in the case of chlorophyll-*a*, by the equation $C_{55}H_{72}O_5N_4Mg + 2CO_2 + 2H_2O = C_{55}H_{74}O_5N_4 + Mg(HCO_3)_2$. Carbon dioxide has therefore the power of breaking the two links between the metal and nitrogen atoms in the molecule.

Before the magnesium is completely removed, however, an important intermediate compound, of the nature of a hydrogen carbonate, is formed. As this has the same colour as chlorophyll,

the subsidiary valency chromophoric complex is still existent, thus:

$$\equiv N \cdot C \vdots C \cdot \overset{\parallel}{C} \cdot N \cdot \overset{\parallel}{C} - \qquad \qquad \equiv N \cdot C \vdots C \cdot \overset{\parallel}{C} \cdot N H \cdot \overset{\parallel}{C} -$$

$$\text{>Mg} \quad + CO_2 + H_2O \rightleftharpoons \quad \text{>Mg} \cdot O \cdot CO_2 H$$

$$\equiv N \cdot C \vdots C \cdot C \cdot N \cdot C - \qquad \qquad \equiv N \cdot C \vdots C \cdot C \cdot N \cdot C -$$
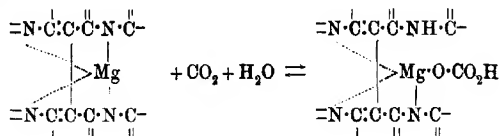
The evidence in favour of the existence of such an intermediate compound is as follows. (1) If a chlorophyll hydrosol is partly saturated with carbon dioxide, then extracted with ether, and the ash of the pigment is estimated, it will be found that the magnesium content is greater than it would be if the gas had directly eliminated the metal. (2) If partly saturated solutions are poured into alcohol (4 parts) and purified air is bubbled through the solution, all the carbon dioxide is recovered and chlorophyll is reproduced.

If the partly saturated hydrosols themselves are allowed to dissociate, however, the carbon dioxide is not quantitatively recovered. Hydrolysis takes place, which in the case of chlorophyll-a results in the quantitative formation of phæophytin and the basic carbonate, $4MgCO_3, Mg(OH)_2$. With chlorophyll-b, a certain amount of chlorophyll is regenerated.

The obvious suggestion is, therefore, that chlorophyll in the leaf unites with carbon dioxide in a similar way, but the conditions are not quite the same. The speed at which carbon dioxide is absorbed by the leaf is much greater than it is in the case of the hydrosol, and the leaf thrives in an atmosphere containing as much as 20% of carbon dioxide, which is a concentration that would very soon lead to the decomposition of chlorophyll in solution. At any rate, the photosynthesis which goes on in the leaf is now to be regarded as an action of the light on the compound of carbon dioxide and chlorophyll, which consists in transforming the carbonic acid into a peroxidic isomeride, capable of parting with oxygen in the gaseous form. Two isomerides are possible, namely, per-formic acid, $H \cdot CO \cdot O \cdot OH$, which is known to change easily into carbonic acid (d'Ans and Frey, A., 1912, i, 601), and a hypothetical peroxide of formaldehyde, $OH \cdot CH \overset{O}{\underset{O}{<}}$ The latter possibility is discussed in the light of the fact that formaldehyde is the primary product in the photosynthesis of carbohydrates.

$$\text{J. C. W.}$$

The Permeability of Living Protoplasm to some Salts. ARTHUR TROENDLE (*Arch. Sci. phys. nat.*, 1918, [iv], **45**, 38—54, 117—132).—Salts in hypertonic solutions are absorbed at first with a constant velocity, characteristic for each salt, but after a certain quantity of the salt has been absorbed, the velocity of entry diminishes steadily. In the first stage there is a definite

ratio between the concentration and the time, and in the second
stage there is a ratio between the concentration and the logarithm
of the time. The entry of salts through living protoplasm does
not obey Fick's law of diffusion. The nature of the cation controls
the velocity of entry of a salt much more than that of the anion.
In a group of chemical elements there is a concordance between
the influence of an ion on the velocity of absorption and its posi-
tion in the periodic classification of the elements. As an explana-
tion of the experimental facts, the author suggests the following
hypothesis. The salts irritate the protoplasm, which replies by
transferring some of the salt to its interior. During this process,
changes of an unknown character, designated by the term
"fatigue," take place in the protoplasm. This fatigue, in in-
creasing, obeys Weber's law.   W. G.

Soluble Carbohydrates in Green Leaves. HARALD KYLIN
(*Zeitsch. physiol. Chem.*, 1918, **101**, 77- 88).—The author
estimates the amounts of various soluble carbohydrates in the
leaves of plants collected at a period when the products of assimila-
tion are at a maximum. *Tulipa sylvestris* and *Narcissus poeticus*
contain 1% of sucrose in the fresh leaf, together with dextrose and
other soluble sugars, but no starch. There is no sucrose or starch
in *Gentiana brevidens*, the place of the latter being taken by an
apparently new saccharide which reduces Fehling's solution,
possesses a lævorotation, and on hydrolysis yields only dextrose.
It is present to the extent of 2·5%, calculated on the fresh leaves.
Hemerocallis fulva, Fritilaria imperialis, Allium victoriale, and
Veratrum nigrum contain from 2 to 3% of carbohydrates soluble
in water, whilst *Scilla sibirica* and *Iris germanica* contain from
1—2%. There are only traces of starch and reducing sugars in
Convallaria majalis, but a considerable quantity of a polysaccharide
of the inulin type, yielding lævulose on hydrolysis with acetic acid.
Of the plants in the leaves of which starch is present, *Hosta
Sieboldiana* and *Tilia europæa*, containing moderate amounts of
starch, also contain 1—2% of soluble carbohydrates, whereas in
Taraxacum officinale, Bunias orientalis, and *Acer platanoides,* con-
taining much starch, there are only traces of saccharides soluble
in water. With the exception of *Convallaria*, the amount of
starch in the leaves is roughly inversely proportional to the amount
of soluble carbohydrates present.   H. W. B.

**Chemical Composition of "Assimilation-secretion" in
Plants.** ARTHUR MEYER (*Ber. Deut. bot. Ges.*, 1918, **35**, 674—680).
—Previous investigations have shown that the globules (assimila-
tion-secretion) occurring in chloroplasts may be differentiated from
fat by microchemical means. They do not become crystalline on
treatment with potassium hydroxide solution, and with strong nitric
acid they exhibit pitting of the surface. They are soluble in
alcohol, ether, or strong acetic acid, are turned brown by osmic
acid, and reduce ammoniacal silver nitrate solution.
The total volume of the "secretion" in 1 kilo. of dark green

leaves of *Tropaeolum majus* is calculated to be approximately 0·5 c.c., and in old leaves of the same plant immediately prior to withering to be 2·14 c.c.   The dried and powdered leaves of *Funkia Sieboldiana* on being heated at 120° gave a turbid distillate which possessed a characteristic odour and reduced ammoniacal silver nitrate solution.

The author assumes that the "assimilation-secretion" contains compounds related to the leaf-aldehyde isolated by Curtius and Franzen (compare A., 1912, ii, 797, 978, 979; 1914, i, 646), but it is also supposed that the "secretion" contains other constituents, since the amount of Δ^α-hexenaldehyde obtained by these investigators is much less than the total volume of the secretion observed by the author.   H. B. H.

The Manganese Content of the Ash of certain Drugs. L. E. WESTMAN and R. M. ROWAT (*J. Amer. Chem. Soc.*, 1918, **40**, 558—562).—Manganese appears to be fairly widely distributed in the vegetable kingdom (compare Hafner and Krist, *Zeitsch. Oesterr. Apoth. Ver.*, 1907, **45**, 387; Pichard, A., 1899, ii, 40; Jadin and Astruc, A., 1913, i, 948; McHargue, A., 1915, i, 48; Headden, *J. Agric. Res.*, 1915, **5**, 349). The manganese content of certain laxative drugs and allied species of plants, for example, *Rhamnus frangula* (alder buckthorn bark), *Cinnamomum cassia cortex* (cassia bark), *Rhamnus purshiana* (cascara sagrada), podophyllin root, senna leaves, rhubarb root, *Rhamnus californica* bark, licorice root, jalap root, *Euonymus atropurpureus* (wahoo bark), cassia pulp, and Barbadoes aloes has been examined; the first two exhibit a higher content of manganese than any similar plant tissue hitherto examined; the figures are somewhat variable, the maximum being 0·067%. In *Rhamnus purshiana*, it is found that the proportion of manganese in the inner third of the bark is about twice as great as in the outer third. When the powdered drugs of the Rhamnaceæ family are extracted with water, approximately one-fourth of the manganese goes into solution.
                                                      D. F. T.

The Degradation of Inulin and of the "Inulides" in Chicory Root. B. GESLIN and J. WOLFF (*Compt. rend.*, 1918, **166**, 428—430. Compare A., 1917, i, 720).—Chicory roots gathered in October or December and stored one month show a change in their inulin and inulide content. A portion of the inulin is converted into inulide, and some of the less readily fermented inulides undergo further degradation and are converted into the more readily fermented inulides.   W. G.

Occurrence of Catechol and Quinol. EDMUND O. VON LIPPMANN (*Ber.*, 1918, **51**, 272).—During the long spell of dry weather at the end of the summer of 1917, the author found deposits of almost pure catechol on the inner surfaces of the bark cast early in the morning by some old plane trees, and quinol

adhering in dense rings to the viscous exudations at the wounds caused by grafting some pear-trees.   J. C. W.

Microchemistry of Plants. VIII. Organic Crystalline Substances in Gentiana germanica. HANS MOLISCH (*Ber. Deut. bot. Ges.,* 1917, **35**, 653—657).—The occurrence of two distinct crystalline substances in the leaves of *Gentiana germanica* is recorded.   The first of these is obtained as a sublimate of yellow, needle-like crystals when the dry leaves are subjected to micro-sublimation at moderate temperatures.   This compound, to which he name *gentiolutein* is given, is insoluble in water, alcohol, glycerol, aqueous chloral hydrate, olive oil, or in 10% solutions of hydrochloric, sulphuric, or acetic acid, but is easily soluble in acetone.   In barium and calcium hydroxide solutions, the crystals become deep brown and also give a transitory, bright bluish-green colour with calcium chloride solutions.   Gentiolutein occurs not only in the leaves, but also in the stems and flowers of the above species, but could not be detected in *G. asclepiadea, G. ciliata,* or *G. pneumonanthe,* although *G. ciliata* yielded a colourless, crystal-line substance, which, however, differed from gentiolutein in its relations to the various solvents.   A second crystalline substance may be observed when, after removal of the epidermis, the leaf is immersed in distilled water, or when it is treated with 10% solutions of hydrochloric, sulphuric, or nitric acid, or with phenol, alcohol, or glycerol.

Evidence is adduced to show that neither of the substances observed is• identical · with gentiopicrin or gentianin; further chemical investigations are required.   H. B. H.

Conversion of Quicklime in Soil. G. HAGER (*J. Landw.,* 1917, **65**, 245—311).—Evidence confirmatory of earlier observa-tions is given to show that when an application of quicklime is made to the soil, only a small proportion of the lime reappears as calcium carbonate.   The remainder is adsorbed by the soil con-stituents, and it is impossible to detect the presence of free calcium hydroxide after even a very short period of digestion.   This adsorption of lime may be due to surface action or to chemical causes, and is regarded as being associated with the observed increased adsorptive power of a soil for other bases, such as potash and ammonia, which results from an application of lime.

The power of a soil for adsorption appears to be related to its content of clay and the presence of unsaturated compounds, and under normal conditions an equilibrium between the absorptive and adsorptive power of the soil carbon dioxide and the soil com-pounds respectively is soon reached.   The action of calcium carbonate is stated to be less rapid than that of calcium oxide, and some months may elapse before an equilibrium is obtained.   The influence of calcium oxide on the physical character of the soil is also discussed.   H. B. H.

The Nitrogen Distribution of Fibrin Hydrolysed in the Presence of Ferric Chloride. CLARENCE AUSTIN MORROW and WALTER RAYMOND FETZER (*Soil Sci.*, 1918, **5**, 163—167).—With the view of obtaining more evidence on the formation of humin nitrogen in soils, fibrin was hydrolysed (1) alone, (2) in the presence of ten times its weight of anhydrous ferric chloride, and the resulting product was, in each case, analysed by the Van Slyke method. The results show that when a protein is hydrolysed in the presence of ferric chloride, an accurate nitrogen distribution cannot be obtained. There is a substantial increase in the ammonia nitrogen (from 10·48 to 13·17%), due to the presence of ferric chloride, owing probably to the higher temperature of hydrolysis, and consequent deamination of some amino-acids. The acid-soluble humin nitrogen increases (from 1·0 to 9·84%) at the expense of a corresponding loss in the filtrate from the bases. The earlier conclusion (compare A., 1917, i, 512) in regard to humin nitrogen precipitated by calcium hydroxide is therefore incorrect, a part of this acid-soluble humin being of protein origin instead of largely non-protein. Emphasis is laid on the fact that much of the recent work on the organic nitrogen distribution in soils by Van Slyke's method is entirely untrustworthy. [See also *Ind.*, May.]

W. G.

The Significance of the Sulphur in Ammonium Sulphate Applied to certain Soils. CHARLES B. LIPMAN and W. F. GERICKE (*Soil Sci.*, 1918, **5**, 81—86).—The superiority of ammonium sulphate as a nitrogenous fertiliser for barley (compare *ibid.*, 1916, **2**, 575) is apparently due to its sulphur content, the sulphur combined with the nitrogen producing the effect. [See, further, *Ind.*, 252A.]

W. G.

Some Availability Studies with Ammonium Phosphate and its Chemical and Biological Effects on the Soil. F. E. ALLISON (*Soil Sci.*, 1918, **5**, 1—80).—A comparison of commercial ammonium phosphate with ammonium sulphate, organic fertilisers, and certain phosphatic fertilisers. Ammonium phosphate nitrifies at approximately the same rate as ammonium sulphate, whilst organic nitrogenous manures, such as dried blood and cottonseed meal, are much less available. Calcium carbonate proved favourable to nitrification, but calcium oxide sometimes caused a depression in the nitrification of the two ammonium salts. There was apparently but little difference in the availability of the phosphorus in ammonium phosphate, acid phosphate, and basic slag, but raw rock phosphate was much less available.

For details of manufacture of the ammonium phosphate and comparative cropping tests with the various fertilisers, see *Ind.*, 252A.

W. G.

General and Physical Chemistry.

Determination of the Carrier in the Emission of the Continuous Spectrum by the Hydrogen Canal Rays. J. STARK, M. GÖRCKE, and M. ARNDT (*Ann. Physik*, 1917, [iv], **54**, 81—110. Compare A., 1917, ii, 281).—The conditions under which the ultra-violet continuous spectrum is emitted by hydrogen canal rays have been investigated, and an attempt is made to identify the entities which are directly responsible for this radiation.

The intensity of the continuous spectrum increases as the wavelength diminishes from $\lambda\,400$ to $\lambda\,240$, and the increase is particularly marked in the region from $\lambda\,280$ to $\lambda\,240$. The distribution of the intensity is independent of the velocity of the hydrogen canal rays.

The continuous spectrum is emitted by the hydrogen canal rays in oxygen, and the intensity of this spectrum, as well as the distribution of the intensity, are the same as for the spectrum emitted by the canal rays in hydrogen. A continuous spectrum is also emitted by nitrogen canal rays in nitrogen and by oxygen canal rays in oxygen, but for cathode falls of potential varying from 800 to 8000 volts, the intensity of this spectrum is less than one-tenth of the intensity of the continuous spectrum emitted by the hydrogen canal rays. Nitrogen canal rays in hydrogen give rise to the emission of the hydrogen series lines in considerable intensity, but there is no appreciable continuous radiation even when the cathode fall of potential reaches 8500 volts.

From these observations, the conclusion is drawn that the emission of the continuous spectrum in question is characteristic of hydrogen. The facts suggest that the radiating entity is neither the hydrogen ion nor the neutral hydrogen atom, but that the continuous spectrum is due to an intermediate type in which the hydrogen ion is combined or associated with an electron, the combination representing a transition phase in the reversible change $H + \odot \rightleftharpoons H$. H. M. D.

Experimental Facts and Bohr's Theory of the Hydrogen Spectra. J. STARK (*Ann. Physik*, 1917, [iv], **54**, 111—116).—A theoretical paper in which the author discusses recent observations on the continuous ultra-violet hydrogen spectrum in relation to Bohr's theory. The experimental evidence adduced in support of the view that the entities responsible for the emission of the continuous spectrum contain a single atom of hydrogen (compare preceding abstract) is considered to prove the untenability of Bohr's theory in its present form. Bohr's model of the hydrogen molecule is also incapable of affording an account of the facts which

have led the author to the opinion that the many-lined spectrum is attributable to diatomic combinations carrying a single positive charge.   H. M. D.

Measurements in the Spectrum of Molybdenum according to International Normals. MARTHA PUHLMANN (*Zeitsch. wiss. Photochem.*, 1917, **17**, 97—131).—Measurements of the wave-lengths of lines in the arc spectrum of molybdenum have been made with the aid of a large concave grating. The results obtained for the region λ2420 to λ4888 are recorded and compared with those given by Exner and Haschek. It has been suggested by Paulson that certain pairs of lines exhibit constant frequency differences, but the existence of this relation is not supported by the author's measurements.   H. M. D.

The Arc Spectrum of Tungsten according to International Units. MARIA BELKE (*Zeitsch. wiss. Photochem.*, 1917, **17**, 132—142, 145—168).—Wave-length measurements of the lines in the arc spectrum of tungsten between λ2249 and λ6984 are recorded and compared with the results previously obtained by Exner and Haschek. The existence of pairs of lines with constant differences of frequency is not indicated by the measurements.
    H. M. D.

Colour of Inorganic Compounds. F. RUSSELL VON BICHOWSKY (*J. Amer. Chem. Soc.*, 1918, **40**, 500—508).—A theoretical paper in which an attempt is made to connect the colour of inorganic substances with the valence electrons and the stability of the electron grouping round the positive nucleus.   H. M. D.

The Polymorphism of certain Substances (Liquid Crystals and Sphaerolites with Helicoidal Winding). PAUL GAUBERT (*Bull. Soc. franç. Min.*, **40**, 5; from *Chem. Zentr.*, 1917, ii, 806—807. Compare A., 1916, ii, 604; 1917, ii, 113).—Amyl cyanobenzylideneaminocinnamate has been found to exist in four different crystalline modifications. The stable α-form is biaxial, optically negative, and has a high rotatory power; it is obtained by crystallisation of the fused substance or by evaporation of solutions. The β- and γ-forms are sphærolitic and distinguished by differences in rotatory power; they are obtained by the rapid evaporation of solutions. The fourth modification is that described by Vorländer and Huth (A., 1911, ii, 165).

Anisylideneaminoazotoluene exists in five different crystalline forms, which are all biaxial. The stable α-form is monoclinic or triclinic, and the other four are probably rhombic. There are also two liquid anisotropic forms of this substance, one of which is optically positive and the other negative.

The cholesteryl esters of low freezing point readily form liquid crystals when their solutions are evaporated. A difference in the endency to form solid crystals has been observed according to the tical character of the liquid phase.   H. M. D.

The **Photolysis of Uranium Salts.**   E. BAUER (*Schweiz. Chem. Zeit.*, 1918, **2**, 40—41).—When light is absorbed by a solution of a uranium salt, the uranyl ion undergoes a reversible change from the "dark" condition into the "light" condition; when the reverse action takes place, the light energy absorbed is given off again in the form of fluorescence. The addition of certain substances, such as chlorine or iodine ions, ferric and vanadyl salts, vanadic acid, and quadrivalent uranium salts, extinguishes the fluorescence. The same substances also destroy the Becquerel effect. In the "light" condition, the uranium is resolved into a higher (octavalent) and a lower (tervalent) stage of valency, and the two reunite to the sexavalent form in reverting to the "dark" condition. When an inhibiting substance is added, the formation of the intermediate products is prevented, because they are immediately taken up by the substance, for example, iodine to form the sexavalent ion. Under the influence of light, uranyl formate is decomposed with liberation of carbon dioxide and hydrogen, a reaction in which the octavalent uranyl ion plays a part. The reaction dies down again through the accumulation of the sexavalent ion, which acts as an extinguisher. Another instance of photolysis is the decomposition of oxalic acid by uranyl sulphate under the action of light. In this case, the octavalent intermediate ion produces carbon dioxide and the tervalent ion carbon monoxide, whilst the sexavalent ion is reconstituted. Analogous processes of simultaneous oxidation and reduction are held to account for the photosensitising effects of other fluorescent compounds, such as eosin.   J. F. B.

The **Photolysis of Uranyl Formate.**   E. C. HATT (*Zeitsch. physikal. Chem.*, 1918, **92**, 513—562).—The decomposition of solutions of uranyl formate under the influence of light has been further examined with a view to the determination of the influence of the concentration of the uranyl salt, the intensity of the light, and the presence of foreign substances.

The experiments with varying concentration indicate that the photolysis is retarded by the uranous salt, which is one of the products of the light reaction. For widely varying light intensities, the initial velocity of the reaction is proportional to the intensity of the light, but at later stages the velocity increases less rapidly than the intensity of the acting light. Potassium chloride, potassium iodide, ferric chloride, vanadyl sulphate, and vanadic acid retard the reaction, but potassium sulphite appears to produce no change in the velocity of the reaction. The view that uranium compounds of higher and lower valency are formed is rendered probable by the fact that the insolated solutions have an oxidising action on potassium iodide and a reducing action on potassium permanganate. In terms of the oxidation and reduction products, it is possible to explain a number of facts which have been established in this and previous investigations of the photochemical decomposition of uranyl formate (compare A., 1916, ii, 9).

A method for the estimation of uranous salts in presence of formic acid is described. The uranium solution acidified with sulphuric acid is added to a solution containing ammonium acetate and sodium phosphate placed in a cylindrical separating funnel connected below with a suction pump through a filter bottle. The funnel is provided with a Gooch filter and with an attachment by which the air in the funnel can be replaced by hydrogen. The mixture of uranyl ammonium phosphate and uranous phosphate which is precipitated, is filtered by suction in the hydrogen atmosphere, the precipitate washed with ammonium acetate solution and then dissolved in sulphuric acid (1:4), the solution thus obtained being titrated with standard permanganate. This method of estimating uranous salts has been found to give quite satisfactory results in the investigation of the insolated urany formate solutions.   . H. M. D.

The Scattering of α-Rays as Evidence on the Parson Magneton Hypothesis. DAVID L. WEBSTER (*J. Amer. Chem Soc.*, 1918, **40**, 375—379).—The large-angle scattering of α-rays is generally considered to prove the untenability of theories of atomic structure which postulate large diffuse spheres of positive electricity. The magneton hypothesis, put forward by Parson (*Smithsonian Miscellaneous Collections*, 1915, **65**, No. 11), postulates such a structure, but the author contends that this is not really an essential feature, and that the α-ray scattering cannot be accepted as valid evidence against the magneton theory.   H. M. D.

Absorption Laws for Röntgen Rays. R. GLOCKER (*Physikal Zeitsch.*, 1918, **19**, 66—72).—This paper contains a discussion of the laws expressing the absorption coefficient of X-rays as a function of the wave-length and atomic number of the absorbing element, and contains tables of the various constants involved in the formulæ for ten elements and six compounds. The data are of practical and theoretical importance, but the paper cannot be suitably abstracted.   F. S.

X-Ray Spectra and the Constitution of the Atom. L. VEGARD (*Phil. Mag.*, 1918, [vi], **35**, 293—326).—An account of work previously described (compare this vol., ii, 93, 94). The periodic variation of the electric conductivity of the elements (Benedicks, *Jahrb. Radioaktiv. Elektronik*, 1916, **13**, 362) is considered to afford support for the configurations which are put forward by the author.   H. M. D.

Solubility of Pure Radium Sulphate. S. C. LIND, J. E. UNDERWOOD, and C. F. WHITTEMORE (*J. Amer. Chem. Soc.*, 1918 **40**, 465—472).—If a solution containing a mixture of radium and barium salts is partly precipitated by the addition of a sulphate the ratio of radium to barium in the precipitate is the same as in the original solution. The behaviour resembles that which is met

with in the case of the isotopic elements, and has not yet been satisfactorily explained. With the object of providing data which may serve to elucidate the nature of the phenomenon, the authors have determined the solubility of pure radium sulphate in water and in sulphuric acid solutions.

The measurements were made by dissolving the salt and also by precipitating it from solution. The mean value obtained for the solubility in water at 25° is 2.1×10^{-8} gram per c.c., which is about one-hundredth of the solubility of barium sulphate. The presence of sulphuric acid up to 50% has no appreciable influence on the solubility. At higher acid concentrations, the solubility increases rapidly, the data obtained showing that the solubility is more than twelve times as great in 70% acid as in 60% acid. In dilute acid solutions, the solubility increases about 50% when the temperature is raised from 25° to 35°, and the same increase is found when the temperature is raised to 45°. The observed value of the solubility of radium sulphate is in agreement with that expected from a comparison of the solubilities of the sulphates of calcium, strontium, and barium.

The term pseudo-isotopy is given to the phenomenon which is exhibited by radium and barium sulphates.   H. M. D.

Radioactivity of the Lake of Rockange. (Miss) H. J. Folmer and A. H. Blaauw (*Proc. K. Akad. Wetensch. Amsterdam,* 1918, **20**, 714—735).—A detailed account is given of the investigation of the radioactivity of samples of mud obtained by borings to different depths from the floor of the lake of Rockange (Hook of Holland). In contradiction to certain previous observations, the authors' results lead to the conclusion that the alluvial mud of the lake possesses no radioactivity of importance. The figures obtained correspond with an average value of the order of 10^{-12} gram of radium per gram. With regard to the origin of this, it is suggested that the radioactive substance in the mud is for the most part brought down by the rivers and does not come from the dunes.   H. M. D.

Electrical Conductance of Solutions in Bromine. Edward H. Darby (*J. Amer. Chem. Soc.,* 1918, **40**, 347—356).—Trimethylammonium chloride is readily soluble in liquid bromine, producing solutions of a yellow colour, the viscosity of which increases very rapidly with the concentration. The electrical conductivity of these solutions has been measured at 18° with results which show that the equivalent conductance of the salt increases from 0.3186 at $c=0.09076$ gram-equivalents per litre to 11.49 at $c=1.2356$. The variation of the conductance with the concentration is in agreement with the equation of Kraus and Bray. The constants have values which are comparable with those obtained for electrolytes in other solvents.

The conductance of trimethylammonium chloride is much greater than that obtained for iodine and phosphorus pentabromide,

the conductance of which in liquid bromine has been previously examined by Plotnikov and Rokotjan (A., 1913, ii, 378).

H. M. D.

The Influence of some Hydroxy-acids on the Electrical Conductivity of Boric Acid. J. Böseken and H. Kalshoven (*Rec. trav. chim.*, 1918, **37**, 130—143).—In continuation of previous work (compare A., 1916, ii, 73, 209), the authors have examined the influence of glycollic, α-hydroxy-β-phenylpropionic, β-hydroxy-β-phenylpropionic, and diglycollic acids on the electrical conductivity of boric acid. Glycollic acid gave an increase in the conductivity, but the substitution of a group ·O·CH₂·CO₃H for the hydroxyl group changed the influence from positive to negative, as shown by the results with diglycollic acid. β-Hydroxy-β-phenylpropionic acid is similar to β-hydroxybutyric acid (*loc. cit.*) in its influence. The influence of α-hydroxy-β-phenylpropionic acid is positive and almost equal to that of lactic acid (*loc. cit.*).

W. G.

The Influence of some Derivatives of Nitrogen on the Electrical Conductivity of Boric Acid. J. Böseken [with W. Sturm and G. Goettsch] (*Rec. trav. chim.*, 1918, **37**, 144—161).—The nitrogenous compounds examined were carbamide, biuret, alloxan, alloxantin, glycine, glutamic, cyanuric, and dialuric acids, dihydroquinazoline (quinoxaline), and the glycol of uric acid. The results indicate that the presence of the group ·NH·CO· has no influence on the electrical conductivity of boric acid, and that substances containing this group do not form complexes with boric acid. The results obtained with quinoxaline favour the ketonic formula $C_6H_4\diagdown^{NH \cdot CO}_{NH \cdot CO}$ for this compound.

Glycine forms a complex boric acid derivative, which is, however, dissociated to a large extent, judging from the slight increase in conductivity obtained. Alloxan in aqueous solution has $K < 5 \times 10^{-9}$, and it does not form a complex with boric acid. Dialuric acid does not form a complex with boric acid. It has $K = 6 \times 10^{-5}$, the value diminishing rapidly, probably owing to oxidation. Alloxantin dissociates in aqueous solution into dialuric acid and alloxan. The glycol of uric acid slightly increases the conductivity of boric acid.

W. G.

The Influence of Boric Acid on the Electrical Conductivity of Diacetyl. J. Böseken [with G. van der Hoek Ostende] (*Rec. trav. chim.*, 1918, **37**, 162—164).—The results obtained, although incomplete, indicate that, in concentrated solution, diacetyl is dihydrated. It has an acid reaction in aqueous solution, having $K = \pm 4 \times 10^{-7}$.

W. G.

The Influence of some Hydroxy-acids on the Electrical Conductivity of Boric Acid. J. Böseken [with (Mlle.) J Weisfelt, (Mlle.) J. van der Spek, Chr. van Loon, and G Goettsch] (*Rec. trav. chim.*, 1918, **37**, 165—178. Compare preceding abstract).—Four acids were studied. α-Hydroxyoctoic acid

like other α-hydroxy-acids, gives with boric acid a complex having a high conductivity. Glyceric acid behaves like an α-hydroxy-acid, the β-hydroxyl group having no influence on the conductivity. Dihydroxymaleic acid behaves in aqueous solution like a di-α-hydroxy-acid. Its decomposition is retarded by boric acid. With fluconic acid, the increase in the conductivity is greater than that with the other α-hydroxy-acids, the group $:C(OH)\cdot CO_2H$ exerting its influence in addition to that of the four other hydroxyl groups. The opening of the lactonic ring may be followed by the regular change in the conductivity, which increases with increase in the concentration of the hydrogen ions.   W. G.

The **Influence of Boric Acid on the Conductivity of some Optically Active α-Hydroxy-acids, and on that of their Racemates.** J. BÖESEKEN and L. A. VAN DER ENT (*Rec. trav. chim.*, 1918, **37**, 179—183).—Measurements of the electrical conductivity of *r*- and *d*-amygdalic acids and *r*- and *d*-tartaric acids in the presence of boric acid show that the influence of a racemic acid on the electrical conductivity of boric acid is equal to that of its active component.   W. G.

Free Energy of Dilution of Sulphuric Acid. MERLE RANDALL and O. E. CUSHMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 393—397).—The *E.M.F.* of cells of the type $H_2|H_2SO_4|Hg_2SO_4|Hg$ has been measured for widely varying sulphuric acid concentrations. From the results, the authors have calculated the free energy of the reaction $H_2 + Hg_2SO_4 = H_2SO_4 + 2Hg$ for acids of different concentration. In combination with previous data (compare A., 1914, ii. 521), these results also give the free energy of formation of sulphuric acid from $1N$ hydrogen and sulphate ions. The numbers obtained are tabulated.   H. M. D.

Electromotive Force and Free Energy of Dilution of Lithium Chloride in Aqueous and Alcoholic Solutions. J. N. PEARCE and F. S. MORTIMER (*J. Amer. Chem. Soc.*, 1918, **40**, 509—523).—The influence of the solvent on the *E.M.F.* of concentration cells has been systematically examined in experiments with solutions of lithium chloride in water and the five lowest alcohols of the series beginning with methyl alcohol. The concentration ratio was in all cases 10:1, the absolute concentration of the stronger solution varying from 1·0 to 0·05 mol. of lithium chloride per litre.

The data recorded are those obtained with cells of two types. In the case of cells involving transference, the *E.M.F.* increases with increasing dilution in water and the three lower alcohols, but decreases with dilution in *n*-butyl and *iso*amyl alcohols. For cells arranged so that there is no transference, the observed *E.M.F.* decreases with increase in the dilution in all the solvents examined. These relations indicate that the ionisation of lithium chloride is abnormal in all these solvents.

The transport number of the lithium ion, the free energy of dilution, and the activity ratios for both the ions and the non-ionised molecules, have been calculated. The transport number increases with the dilution, whilst the free energy of dilution and the activity ratios decrease with the dilution in all the solvents examined.

An attempt is made to account for these relations by the assumption of effects due to hydration, polymerisation, and change in the dielectric capacity of the solvent.   H. M. D.

Effect of Interionic Force in Electrolytes. II. S. R. MILNER (*Phil. Mag.*, 1918, [vi], **35**, 352—364. Compare this vol., ii, 54). -The author's view, that the decrease in the molecular conductivity of electrolytes with increasing concentration is to be attributed mainly to a reduction in the mobilities of the ions, and not to a reduction in their number by their combination to form molecules, is discussed further by reference to the influence of interionic forces on the electrical conductivity and on the osmotic pressure. The theoretical investigation of this influence leads to the conclusion that a change in the concentration will produce identical variations in the conductivity and in the osmotic pressure of the free ions, that is to say, the ions which momentarily have no mutual energy with other ions.

This result, when applied to strong electrolytes, suggests that the observed changes in the conductivity and osmotic pressure of strong electrolytes with the concentration may be explained by a modification of the usual view. Interionic forces produce an increase in the frequency of occurrence of ions in an associated state, and the result of this is a reduction in the osmotic pressure of the free ions. The average mobility of an ion, taken over a period sufficiently long to include it in the free and associated state, is reduced in the same ratio, and the experimental facts are thus accounted for. If this view is correct, the ions of strong electrolytes are not associated into molecules, but pairs of oppositely charged ions which are temporarily in closest proximity will behave in a certain number of cases as if they were bound together.

H. M. D.

Alternating Current Electrolysis with Mercury Electrodes. HARRY B. WEISER (*J. Physical Chem.*, 1918, **22**, 78—94). —When solutions of sodium thiosulphate are subjected to the action of an alternating current between metallic electrodes, metallic sulphides are precipitated in quantities which increase as the frequency of alternation decreases. The extent to which the electrodes are thereby corroded varies considerably with the nature of the electrode surface, and reproducible results cannot be obtained with solid metals.

When mercury electrodes are used, the changes in the surface tension give rise to a rhythmical vibration of the mercury surface which maintains the electrode in its original condition and serves

to agitate the solution in the immediate neighbourhood of the electrode. In these circumstances, reproducible results are obtained, and experiments have been made in which the same frequency of alternation was used (72000 alternations per minute), but in which changes were made in the current density, the temperature, and the concentration of the sodium thiosulphate solution.

The corrosion of the mercury electrodes increases with the current density, but not in direct proportion. The departure from proportionality is greater in the more dilute solutions. The corrosion also increases with the concentration of the thiosulphate solution, the two quantities being approximately proportional. When the concentration reaches a certain limit, a film of sulphide is formed over the mercury surface, and this greatly reduces the corrosion. The corrosion increases with rise of temperature and is increased by mechanical stirring.

Under like conditions, zinc electrodes are corroded to a much smaller extent, and although it is probable that the above factors affect the degree of corrosion, as in the case of mercury, variations in the electrode surface have a much greater influence on the actual result.   H. M. D.

Thermal Leakage and Calorimeter Design. WALTER P. WHITE (*J. Amer. Chem. Soc.*, 1918, **40**, 379—393).

—The factors which play a part in the interchange of heat between a calorimeter and its environment are considered, more particularly with reference to the influence of the surrounding air. The convection currents in this air are of considerable importance in that the thermal leakage due to convection is approximately proportional to the square of the difference between the temperatures of the calorimeter and its environment. The influence of convection may be diminished by reducing the width of the air gap round the calorimeter. It is shown that gaps of from 10 to 17 mm. are most suitable for ordinary calorimeters, but larger gaps may be used in the case of large calorimeters in which smaller temperature differences are involved. Thin reflecting shields may be advantageously employed to diminish the effect of conduction.
·H. M. D.

Specific Heats at Low Temperatures of Sodium, Potassium, Magnesium, and Calcium Metals and of Lead Sulphide. E. D. EASTMAN and W. H. RODEBUSH (*J. Amer. Chem. Soc.*, 1918, **40**, 489—500).

—On the assumption that $C_v = 3R$ is the normal higher limit for the atomic heat of an element, it would seem that the strongly electropositive metals have exceptionally large atomic heat capacities, and in order to obtain further information on this point, measurements have been made of the specific heats of sodium, potassium, magnesium, and calcium between 65° and 300° (abs.).

The method used consisted in measuring the rise of temperature

produced by a known quantity of electrical energy supplied to the metal suspended in a vacuum, the change of temperature being measured by means of a carefully calibrated copper–constantan thermocouple. From the values of C_p derived from the experimental data, the values of C_v were obtained by calculation according to methods previously described.

The results obtained show that the value of C_v becomes considerably greater than $3R = 5.97$ cal. over the higher portion of the range of temperatures examined. According to Lewis and Gibson (*J. Amer. Chem. Soc.*, 1917, **39**, 2554), the curve which is obtained by plotting C_v against the logarithm of the absolute temperature is a general curve which can be made to fit the data for any one of a large number of elements by simple horizontal displacement. When the data obtained by the authors are examined in reference to this general curve, it is found that the points for sodium, magnesium, and calcium lie on the curve at lower temperatures, but are situated above it at the higher temperatures. In the case of potassium, the values of C_v lie above the curve at all temperatures examined.

The deviations from the normal curve are considered to be due to the heat capacities of the electrons, the energy absorption of which is supposed to depend on the degree of constraint to which they are subjected in the atom. This constraint diminishes with increase in the electropositive character of the metal.   H. M. D.

Boundaries of Existence of the Liquid State. W. HERZ (*Zeitsch. Elektrochem.*, 1918, **24**, 48—50).—The author has collected and tabulated the melting points and critical temperatures of a number of elements, halogen derivatives of non-metals, and some organic compounds. It is shown on comparison that in the case of metals the region of existence of the liquid decreases with increasing atomic weight in a given group of the periodic system, whilst for non-metals the region of existence increases. The same regularity holds for the halogen derivatives of the non-metals. In the case of organic compounds, the region of existence of the liquid increases with increasing molecular weight. The quotient, critical temperature/melting point, is approximately a constant for analogous groups of substances (see also Clarke. *Amer. Chem. J.*, 1896, **18**, 618).   J. F. S.

The Cryoscopic Constant of Asymmetric Heptachloropropane, $CCl_3 \cdot CCl_2 \cdot CHCl_2$. J. BÖESEKEN and J. BENEDICTUS (*Rec. trav. chim.*, 1918, **37**, 121—129).—Determinations have been made with a large number of different substances, and the results show that the heptachloropropane has a cryoscopic constant just under 120, but the solubility in it of hydroxy-compounds and acids is not very great. Acids are strongly associated in this solvent, even acids of high molecular weight, giving values equal to twice the theoretical molecular weight. Alcohols at great dilutions give almost normal molecular weights, but as the concentra-

on increases they become associated. Hydrocarbons, chloro-compounds, amines, and esters behave normally. W. G.

Formula giving the Saturated Vapour Pressure of a diatomic Liquid. E. ARIÈS (*Compt. rend.*, 1918, **166**, 447—450. Compare this vol., ii, 61).—The author deduces the formula $[=r^{0.4}Z/x$, where $x=[1+\{(1-\tau)(0\cdot86-\tau)\}/(0\cdot353\tau^2+0\cdot642)]\tau^{\frac{7}{4}}$, and shows that the calculated results agree with the observed results in the cases of chlorine and carbon monoxide. W. G.

The Anomalies which the Saturated Vapour Pressures of certain Diatomic Liquids Show. E. ARIÈS (*Compt. rend.*, 1918, **166**, 553—556).—The formula previously deduced from a study of chlorine and carbon monoxide (preceding abstract) applies also to hydrogen chloride and hydrogen iodide, but in the cases of oxygen, nitrogen, and nitric oxide certain anomalies occur between the values as calculated and observed. W. G.

Thickness and Structure of the Capillary Layer of a Liquid in Contact with its Saturated Vapour. G. BAKKER (*Ann. Physik*, 1917, [iv], **54**, 245—295).—By making use of the Laplacian theory of capillarity and certain thermodynamic arguments, it is shown that the number of molecules in the surface layer increases from about three at the freezing point of the liquid to a very much larger number in the neighbourhood of the critical temperature. In the case of carbon dioxide at the reduced temperature $0\cdot999°$, the number obtained lies between 300 and 1800. Thermodynamic reasoning leads to the conclusion that the thickness of the surface layer is about $1\cdot5\,\mu\mu$ at the reduced temperature $0\cdot9°$, whilst in the immediate neighbourhood of the critical temperature the thickness increases to a value represented approximately by half the wave-length of violet light. The thermodynamic method gives results which agree with those previously mentioned in so far as the number of molecules in the surface layer is concerned.

Since the number of molecules in the surface layer is very limited if the temperature is not in the neighbourhood of the critical temperature, it follows that the radius of action of the attractive forces does not extend beyond the limits of the nearest molecules. This deduction is not compatible with the assumptions involved in the original theory of Laplace. H. M. D.

The Law of Thermochemical Processes (Summary) and of Photochemical Processes. MAX TRAUTZ (*Zeitsch. anorg. Chem.*, 1918, **102**, 81—129).—According to the author's theory, reactions in gases take place only between molecules which are in an "activated" condition. A species of thermal isomerism of the molecule is assumed, and the heat energy necessary to transform the inactive into the active modification is termed the "heat of activation." In the mass-action equations developed from thermodynamic principles for reactions of the first and second orders, the

factor representing the heat of activation appears as an exponential function, and from two determinations of the velocity constant of a reaction at two different temperatures, it is possible to calculate the heat of activation. The heat of activation is a fraction of the total heat of decomposition into atoms, and this fraction can be calculated from the heat of reaction and the heat of activation. In the case of the reaction $H_2 + I_2 \rightleftharpoons 2HI$, for instance, the fraction is between one-fourth and one-third.

According to the author's theory, the time of contact between two "activated" molecules is of so short duration that the chance of simultaneous contact with a third activated atom is very small indeed. Reactions of a higher order than the second are therefore held to be impossible (compare A., 1915, ii, 338, 623, 828; 1916, ii, 304, 422).

The theory is applied to photochemical reactions, and equations are given for reactions of the first and second orders. The relation of the heat of activation to the frequency of the actinic radiation is considered, with special reference to Planck's radiation law, which is deduced in a novel manner. Just as the course of a thermochemical reaction is determined by the smallest heat of activation, to the exclusion of those reactions requiring greater heats of activation, so a photochemical reaction is determined by the smallest radiation frequency to which the substance is resonant. The relation between heat of activation and radiation frequency is expressed by an equation $q = R\beta v$, where q is the heat of activation and v is the frequency proper to the reaction. This frequency should be found in the spectrum of the reacting substances, and the possibility arises of determining heats of reaction and heats of activation spectroscopically. The theory is examined in its relation to Bunsen and Roscoe's law and the law of photochemical equivalents.   E. H. R.

The Energy Theory of Matter. H. STANLEY REDGROVE (*Chem. News*, 1918, **117**, 145—146. Compare A., 1917, ii, 411). —In a recent paper (A., 1917, ii, 164), Thornton pointed out that a constant is obtained if the molecular heats of combustion of saturated hydrocarbons are divided by the corresponding numbers of oxygen atoms which are required for the complete combustion of the hydrocarbons. An attempt has been made (Vliet, this vol., ii, 98) to utilise this relation in the calculation of the contribution of the carbon and hydrogen atoms and the valency bonds towards the heats of combustion of their compounds. It is shown that the equation thus introduced is deducible from the equations given by the author, and thus affords no additional basis for the calculations in question.

The author criticises the significance of the relation indicated by Thornton, and contends that it is not generally applicable to different groups of organic compounds.

The advantages of the author's theory as a basis for the computation of additive or partly additive properties are discussed in relation to other underlying hypotheses.   H. M. D.

Equilibria Involving Cyanogen Iodide. The Free Energy of Formation of Cyanogen. GILBERT N. LEWIS and DONALD B. KEYES (*J. Amer. Chem. Soc.*, 1918, **40**, 472—478).—The reversible reactions represented by $2CNI \rightleftharpoons (CN)_2 + I_2$ and $CNI + HI \rightleftharpoons HCN + I_2$ have been examined, and from the equilibrium data the free energy of formation of cyanogen has been calculated.

The partial pressure of iodine in the saturated cyanogen iodide vapour was determined colorimetrically by comparison of this·with the vapour given off by pure solid iodine, the temperature of which was adjusted until the colours in the two comparison tubes were equal. The partial pressure obtained in this way increases from 3·42 mm. at 90·0° to 56·7 mm. at 123·0°. From these partial pressures, the equilibrium constant is calculated, and the logarithms of these numbers when plotted against the reciprocal of the absolute temperature fall very nearly on a straight line, from the slope of which the heat absorbed in the dissociation is found to be 48,000 cal. By extrapolation, the value of the equilibrium constant at 25° is obtained, and this leads to $\Delta F_{298} = 14,950$ for the free energy of the reaction represented by $2CNI(solid) = (CN_2) + I_2(gas)$.

When a mixture of solid cyanogen iodide and iodine is treated with a dilute solution of hydriodic acid, the equilibrium represented by $CNI + H^{\cdot} + I' \rightleftharpoons HCN + I_2$ is quickly established, and methods are described by which the authors have found it possible to obtain the concentrations of the hydrogen and iodine ions and that of the hydrocyanic acid for a series of hydriodic acid solutions of varying strength. The values obtained for $K = \lceil HCN \rceil / [H^{\cdot}][I']$ are not very constant, but by taking the mean value $K = 13$, the free energy of the reaction $CNI(solid) + H^{\cdot} + I' = HCN(gas) + I_2(solid)$ is found to be $\Delta F_{298} = -1520$.

Measurements of the partial pressure of hydrogen cyanide for aqueous solutions of varying concentration gave $P/m = 0.096$ at 25°, where P is the pressure in atmospheres and m the concentration in mols. per 1000 grams of water. From this ratio of distribution, the value $\Delta F_{298} = 1390$ is obtained for the reaction $HCN(aq.) = HCN(gas)$. By combining these with values previously obtained, the free energy of formation of cyanogen iodide according to the equation $C(gas) + \frac{1}{2}N_2 + I(solid) = CNI(solid)$ is found to be $\Delta F_{298} = 38,635$.

Combining this result with the equations for the free energy of dissociation of cyanogen iodide (see above) and the formation of iodine vapour from solid iodine, the free energy of formation of cyanogen gas according to the equation $2C(gas) + N_2 = (CN)_2(gas)$ is found to be $\Delta F_{298} = 87,580$. H. M. D.

The Oxidising Power of Cyanates and the Free Energy of Formation of Cyanides. GILBERT N. LEWIS and THOMAS B. BRIGHTON (*J. Amer. Chem. Soc.*, 1918, **40**, 482—489).—The experiments described were undertaken with the object of providing data for the calculation of the free energy of formation of hydrogen

cyanide, a substance which is of considerable importance in connexion with the determination of the free energy changes associated with many different types of organic reactions.

Fused potassium cyanide is oxidised by carbon dioxide, and the fused cyanate is reduced by carbon monoxide. The equilibrium condition resulting from these opposed reactions has been examined by determining the value of $K = [CO_2]/[CO]$ for the gas mixture in equilibrium with the eutectic mixture of potassium cyanide and potassium cyanate at various temperatures between $721°$ and $847°$ (abs.). Preliminary experiments showed that the eutectic temperature is $555°$ (abs.), and that the mixture contains $14·6\%$ of potassium cyanide. When the values of K are plotted against $1/T$, a straight line is obtained, and by extrapolation to the temperature of the eutectic point this gives $K = 0·89$. From this value of K, the free energy of the reaction $KCNO(solid) + CO(gas) = KCN(solid) + CO_2(gas)$ is found to be $\Delta F_{555} = 126$. This, in combination with the value for the heat of the reaction at the ordinary temperature $\Delta H = 4300$ cal., gives $\Delta F_{298} = 2060$ for the free energy of the reaction at $25°$.

From solubility and freezing-point data, the free energy change associated with the conversion of the solid salts into the corresponding ions in normal concentration has been found to be $\Delta F_{298} = -2130$ for potassium cyanide and $\Delta F_{298} = -1440$ for potassium cyanate. By combination of these results with the previous one, the free energy of the change $CNO' + CO(gas) = CN' + CO_2(gas)$ is found to be $\Delta F_{298} = 1370$.

From this and free energy values previously derived, it follows that for the reaction $C(gas) + \frac{1}{2}N_2 + \odot = CN'$, $\Delta F_{298} = 35,277$, and since the free energy of formation of the hydrogen ion is taken as zero, we have for $\frac{1}{2}H_2 + C(gas) + \frac{1}{2}N_2 = H^{\cdot} + CN'$, $\Delta F_{298} = 35,277$. This result, in combination with $\Delta F_{298} = 11,856$ for the free energy of the reaction $HCN(aq.) = H^{\cdot} + CN'$, gives for the free energy of formation of hydrogen cyanide in accordance with the equation $\frac{1}{2}H_2 + C(gas) + \frac{1}{2}N_2 = HCN(aq.)$ the value $\Delta F_{298} = 23,421$.

H. M. D.

Gas Dilatometer for ascertaining Decomposition Points.

W. C. MOORE and J. B. DAVIES (*Met. and Chem. Eng.*, 1918, **18**, 301—304).—The substance examined is heated in a vacuous glass test-tube placed vertically in a paraffin bath. Distillation products pass into a horizontal pipette-shaped air condenser sealed on to the test-tube and closed at the other end by a U-shaped manometer filled with mercury. The pressure in the apparatus is plotted as the temperature rises. A discontinuity in the curve due to the rapid evolution of permanent gas is taken as the decomposition point. The results are influenced by rate of heating, but when this was 1° per minute up to 150° and then slower, the following results were obtained: sucrose 178°, dextrose 177°, and soluble starch 214°, whilst with cellulose (filter paper) a slow decomposition commenced at 143°, with further points at 185° and 204°.

H. J. H.

Compressibility and Dilatability of Gases. A. LEDUC (*Ann. physique*, 1918, [ix], **9**, 5—28).—A detailed description of a piezo-meter which can be used to observe the gases successively at pressures of 1, 2·8, and 5 atmos., which has been used for neon and argon. The following are the values of the constants found for neon: coefficient of departure from Mariotte's law, $-6 \cdot 10^{-6}$ per cm. of mercury at 17° between 1 and 5 atmos.; molecular volume at 0° and 760 mm., 1·0004; atomic weight, 20·15; coefficient of dilatation, $\beta = 3664 \cdot 10^{-6}$ between 5° and 30°. For argon the values are: coefficient of departure from Mariotte's law, $10 \cdot 2 \cdot 10^{-6}$ between 1 and 5 atmos.; molecular volume, 0·9990 at 0° and 760 mm.; atomic weight, $39 \cdot 91 \pm 0 \cdot 01$; coefficient of dilata-tion, $\beta = 3669 \cdot 10^{-6}$ between 8° and 32°.   W. G.

Fluidity and Specific Volume of Aqueous Solutions. W. HERZ (*Zeitsch. anorg. Chem.*, 1918, **102**, 173—176. Compare A., 1917, ii, 361).—Curves are given showing that, for aqueous solutions of a number of acids, for example, sulphuric and acetic, alkalis such as sodium and potassium hydroxides, hydrolysed salts such as sodium carbonate and ferric chloride, and neutral sub-stances such as sucrose, there is a direct proportionality between the fluidity expressed in *C.G.S.* units and the specific volume. Even in the case of mixed solutions, for example, a solution con-taining sodium and copper sulphates, the proportionality holds.

E. H. R.

Soap Solutions. III. VICTOR LENHER and GEORGE H. BISHOP (*J. Physical Chem.*, 1918, **22**, 95—98).—The adsorption of sodium oleate by Ceylon graphite, willow charcoal, and animal charcoal has been examined by filtering a $N/10$-solution through 30 cm. columns of the principal materials. Successive fractions of the filtered liquid were analysed, and the process continued until no further adsorption occurred. The results show that animal char-coal has a much greater adsorbent capacity than wood charcoal, which, in turn, adsorbs sodium oleate more readily than graphite.

H. M. D.

Theory of Dyeing. H. R. KRUYT and (MISS) J. E. H. VAN DER MADE (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 636—641). —The observations recorded by Reinders (A., 1913, ii, 836) have led the authors to investigate further the influence of various salts on the distribution of dyes between water and *iso*butyl alcohol.

Experiments made with crystal-violet, magenta and methylene-blue, and the sodium salts of different acids show that the sequence of the anions, when arranged according to their influence on the distribution of the basic dye, is identical with the lyotropic series. This sequence is no longer found when acid dyes are substituted for the basic dyes.

The influence of salts on the adsorption of dyes by blood char-coal has also been examined. In the case of methylene-blue-B

extra and auramine-O, the order is not that of the lyotropic series, and it is supposed that the electrical charges of the ions have a preponderating influence. With crystal-violet, on the other hand, the sequence of the sodium salts is that of the lyotropic series. [See, further, *Ind.*, 238A.]   H. M. D.

A New Method for the Measurement of the Coefficient of Diffusion of Electrolytes. St. Procopiu (*Ann. Physique*, 1918, [ix], **9**, 96—112).

—In a broad, vertical tube are superposed two layers of different concentration of the same électrolyte, and the variation of a physical or chemical property, at a given distance from the surface of contact with the time is estimated. In this case, the *E.M.F.* between an electrode of the metal contained in the electrolyte and a similar electrode at a much greater distance is studied, and the time taken for it to reach its maximum is determined. Then $D = x^2/2\theta$, where D is the coefficient of diffusion. x is the distance of the first electrode from the surface of contact, and θ is the time taken for the *E.M.F.*, and consequently the concentration at x, to attain its maximum.   W. G.

Experiments on the Manifestation of Osmotic Pressure with Membranes of Chemically Inert Materials. S. L. Bigelow and C. S. Robinson (*J. Physical Chem.*, 1918, **22**, 99—127).

—The experiments described were made with the object of ascertaining whether osmotic effects are exhibited under conditions which seem to preclude the possibility of chemical reaction between the membrane and the solvent. For this purpose, membranes were constructed from silica, graphite, amorphous carbon, copper, silver, and gold in a very finely divided state. These materials were compressed into the form of disks, which served to separate the solvent and solution. A special type of osmotic cell was devised which appeared to be adapted to the use of membranes of this type.

Preliminary results obtained for sucrose solutions (0·5 to 2 molar) are recorded which show that small osmotic effects are exhibited with these chemically inert membranes. By varying the degree of compression of the disks, the diameter of the pores could be altered, and it has been found that such variations are accompanied by a change in the osmotic effect in the sense that this increases with diminution in the size of the pores.

With copper membranes, negative osmotic effects have been observed. Similar results have been previously recorded for kaolin membranes.   H. M. D.

Crystal Structure of the Alums and the Rôle of the Water of Crystallisation. L. Vegard and H. Schjelderup (*Ann. Physik*, 1917, [ii], **54**, 146—164).

—Bragg's method has been applied in the investigation of the crystal structure of the alums by observations on crystals of potassium alum, ammonium alum, iron ammonium alum, and chrome alum. Using the rhodium line

$\lambda = 0.607 \times 16^{-8}$ cm., the authors measured the relative intensities of the spectra of different orders obtained by reflection from the (100), (110), and (111) planes, and from the results have deduced the probable arrangement of the metal, sulphur, and oxygen atoms in the space-lattice system. For a description of the rather complicated structure, the original paper must be consulted.

The crystal model divides the twenty-four molecules of water into six groups, which groups are cubically disposed with reference to the four tetrahedrally arranged atoms of sulphur. The model makes no distinction between the water of crystallisation and the other constituents of the alum. Any hypothesis which would distinguish the water of crystallisation from water of constitution could not be reconciled with the observed relations between the high-frequency reflection spectra. The removal of the water of crystallisation is necessarily accompanied by the destruction of that structure which is characteristic of the hydrated salt.

The zeolites obviously present an attractive material for investigation in regard to the influence of the water content on the crystalline structure, and observations of a preliminary character have been made on chabasite, crystals of which were dehydrated by heating at 200—300°, and examined before and after dehydration by the X-ray method. The results show that the relative intensities of the spectra of different orders are not appreciably altered by the loss of water. The dehydration is, however, accompanied by a diminution in the absolute intensities, and more particularly by a decrease in the sharpness of the maxima.

The assumption that the water molecules do not form an essential part of the space lattice of the zeolite is held to be inadmissible. The facts can be accounted for by the hypothesis that the weakened reflection of the partly dehydrated crystals is due to crystal elements which have not lost water, and retain therefore their original configuration. Crystal elements which have lost water and from which new structures have been formed are presumably orientated in all possible directions, and for this reason play a minor part in the effective reflection of the X-rays.

H. M. D.

In-, Uni- and Bi-variant Equilibria. XVIII.

F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 659—667. Compare A., 1917, ii, 454).—A further discussion of the equilibrium relations in systems of n-components with n-phases at constant temperature with varying pressure. The properties of such systems are very similar to those which have already been described for conditions in which the pressure is constant and the temperature variable. H. M. D.

One-sided Chemical Equilibria.

E. Baur (*Schweiz. Chem. Zeit.*, 1918, ii, 25—26).—When salicylic acid is heated at 200°, it volatilises, and the vapour undergoes partial dissociation into phenol and carbon dioxide. The degree of dissociation is dependent

on the pressure and follows the law of mass action, $P \cdot \alpha^2/1 - \alpha^2 = K = 254 \cdot 9$, where P is the pressure in cm. of mercury and α is the measured degree of dissociation. Although the dissociation is correctly described as an equilibrium, yet no synthesis of salicylic acid from phenol and carbon dioxide can take place in the gaseous condition. Hence the reaction, being irreversible, is a "one-sided" equilibrium. Another instance of a similar phenomenon has been observed in the formation and decomposition of phloroglucinol-carboxylic acid. Phloroglucinol and potassium hydrogen carbonate in aqueous solution give a partial formation of potassium phloro-glucinolcarboxylate. At 50°, the equilibrium is adjustable from both sides and follows the law of mass action. When the velocity of the changes, on the one hand the formation and on the other the decomposition, of the carboxylate is studied in solutions satu-rated with phloroglucinol, it is found that for the expression $V = K(C - C_1)$, where C is the momentary and C_1 the equilibrium concentration of the carboxylate, the value of K is about one-fourth in the formation of its value in the decomposition. This is explained on the ground that the decomposition of the carb-oxylate may take place in two ways, directly and by way of an intermediate ester salt, potassium phloroglucinol carbonate, whereas the formation of the carboxylate can only take place in one way, namely, through this intermediate stage. If this way through the ester salt did not exist, the carboxylate could decompose, but not re-form, yet the limit of the decomposition must be the same as it actually is where both ways are available.   J. F. B.

Reversible Reactions of Sulphur Compounds.   GILBERT N. LEWIS, MERLE RANDALL, and F. RUSSELL VON BICHOWSKY (*J. Amer. Chem. Soc.*, 1918, **40**, 356—362).—An account is given of preliminary experiments which were undertaken with the object of finding reversible reactions suitable for the investigation of the free energy changes of sulphur compounds.

Towards aqueous solutions of various salts, sulphur begins to exhibit considerable reactivity when the mixtures are heated at 150° to 200°. Mercuric, ferric, and stannic salts are quantitatively reduced, and mercurous, cupric, bismuth, and lead salts are slowly but quantitatively precipitated as sulphides. Nitrate, per-manganate, iodate, and bromate ions are reduced to nitric oxide, manganese dioxide, iodine, and bromine respectively. Chlorates appear to be reduced very slowly, but sulphates, periodates, and perchlorates are not acted on at 180°. The reactions in question are probably due to the reversible change $2H_2O + 3S = 2H_2S + SO_2$, the sulphur dioxide being the active reducing agent.

Solid sulphates are reduced by hydrogen at moderate tempera-tures, and the sulphate ion is reducible at about 150° by mild reducing agents.

The investigation of the decomposition of silver sulphite on heat-ing shows that the reaction does not occur in accordance with the equation $Ag_2SO_3 = Ag_2O + SO_2$, but that the solid product of the reaction is either a basic salt or a solid solution. In presence of

water, reaction takes place more rapidly in accordance with the equation $2Ag_2SO_3 = 2Ag + Ag_2SO_4 + SO_2$, this reaction being catalysed by the water. Sulphuric acid is then produced in consequence of the further reaction represented by $Ag_2SO_4 + SO_2 + 2H_2O = 2Ag + 2H_2SO_4$.

The potential of the sulphur dioxide electrode has also been examined by measuring the $E.M.F.$ of the cell $Pt|SO_2|H_2SO_4|Hg_2SO_4|Hg$ for varying concentrations of the sulphuric acid and varying partial pressures of the sulphur dioxide. It has not been possible to find a satisfactory interpretation of the results obtained.

<div align="right">H. M. D.</div>

Equilibrium in the Reaction between Water and Sulphur at the Boiling Point of Sulphur. GILBERT N. LEWIS and MERLE RANDALL (*J. Amer. Chem. Soc.*, 1918, **40**, 362—367).—The equilibrium in the system $2H_2O + 3S = 2H_2S + SO_2$ has been examined at the boiling point of sulphur. The experiments were made in the presence of an excess of sulphur, and in these circumstances the partial pressure of this compound was constant. A weighed quantity of water, enclosed in a thin-walled sealed tube, was introduced into the reaction chamber, consisting of a glass bulb of known capacity, which was heated in the vapour of boiling sulphur. The formation of hydrogen sulphide and sulphur dioxide is accompanied by an increase in the pressure when the volume of the reaction mixture is kept constant, and the pressures required to maintain this condition were measured in a series of experiments in which varying quantities of water were introduced into the reaction bulb. From these pressures, it is possible to calculate the partial pressures of the hydrogen sulphide, sulphur dioxide, and water in the reacting mixture.

Some difficulties were met with by reason of the fact that the water adsorbed by the surface of the glass is partly given off at the temperature of the experiments, but suitable allowance was made for the effect thereby produced.

The results obtained in six experiments gave values of $K = [H_2S]^2[SO_2]/[H_2O]^3$ varying from 0.00088 to 0.00232. The differences between these results are not considered excessive when the multiplication of errors, which the formula involves, is taken into account. The mean value $K = 0.00154$ may be used in the calculation of the free energy of formation of sulphur dioxide.

<div align="right">H. M. D.</div>

Equilibrium in the Reaction between Water and Sulphur at High Temperatures. The Dissociation of Hydrogen Sulphide. MERLE RANDALL and F. RUSSELL VON BICHOWSKY (*J. Amer. Chem. Soc.*, 1918, **40**, 368—375. Compare preceding abstract).—The equilibrium in question has been further investigated at higher temperatures, where free hydrogen is formed by the dissociation of the hydrogen sulphide. The equilibrium mixture contains, therefore, the five gases, water, sulphur, hydrogen

sulphide, sulphur dioxide, and hydrogen. If the dissociation constant of hydrogen sulphide is known, the composition of the equilibrium mixture of· the five gases can be calculated if the original composition of the mixture, the total pressure, and the partial pressure of one of the five gases are determined.

The partial pressure of the hydrogen has been measured by the use of an evacuated platinum bulb inserted into the reaction chamber, into which the hydrogen diffused until the pressure in the bulb became equal to the partial pressure of the hydrogen in the gas mixture. This apparatus was used in the extension of previous measurements of the dissociation of hydrogen sulphide to higher temperatures. The values obtained for $K_p = [\text{H}_2\text{S}]/[\text{H}_2][\text{S}_2]^{\frac{1}{2}}$ when the pressures are measured in atmospheres decrease from 7·98 at 1362° (abs.) to 1·81 at 1667° (abs.). These results agree with the observations of Preuner and Schupp (A., 1909, ii, 977), whose measurements extended to 1405° (abs.).

In the investigation of the more complex equilibrium, a mixture of gases of known composition was obtained by electrolysing a 10% solution of potassium hydroxide in two separate vessels, the oxygen from one or both of which could be passed over boiling sulphur and converted into sulphur dioxide. The currents passing through the electrolysers, which were placed in parallel, were accurately measured and afforded the data for the calculation of the composition of the original mixture. Since the experiments were made at atmospheric pressure, the further quantity required was readily obtained.

The results obtained in experiments at temperatures ranging from 1160° (abs.) to 1645° (abs.) are used in the calculation of the logarithm of the equilibrium constant $K_p = [\text{H}_2\text{O}]^2[\text{H}_2\text{S}]/[\text{H}_2]^3[\text{SO}_2]$, corresponding with the equation $3\text{H}_2 + \text{SO}_2 = 2\text{H}_2\text{O} + \text{H}_2\text{S}$. The value of log K_1 (partial pressures being measured in atmospheres) decreases from 5·93 at 1160° to 2·56 at 1645° (abs.).

H. M. D.

Studies in Esterification. X. The Esterification of Benzoic and the Toluic Acids by Methyl, Ethyl, and Propyl Alcohols. RAYMOND FREAS and E. EMMET REID (*J. Amer. Chem. Soc.*, 1918, **40**, 569—578).—A re-examination of the position of equilibrium attained by various mixtures of methyl, ethyl, or propyl alcohol with benzoic or one of the toluic acids, or by mixtures of the esters with water. The binary mixture, of known composition, was in each case sealed in a glass tube and heated for four or eight days at 200°, the proportion of acid in the final mixture being then estimated and the percentage of equivalent amounts esterified or hydrolysed at equilibrium calculated by the formula given by Faber and Reid (A., 1917, i, 626). Under these conditions, it is found that with mixtures of any pair of the above alcohols and acids, or of one of the esters with water, in varying proportions, the position of equilibrium accords closely, although not exactly, with the law of mass action, this result agreeing with that of Berthelot and Pean de St. Gilles. Of the toluic acids, the

ortho-compound shows the least and the para-compound the highest esterification limit towards methyl alcohol, but the reverse is true of the esterification limits towards ethyl and propyl alcohols; the esterification limit of any one of the four acids is lower towards ethyl alcohol than towards propyl or methyl alcohol, the latter giving the highest value with each of the acids.　　　D. F. T.

The Hydrolysis of Methyl Sulphate and Ethyl Sulphate with Sodium Methoxide or Ethoxide. J. POLLAK and A. BAAR (*Monatsh.*, 1918, **38**, 501—523).—Methyl sulphate undergoes hydrolysis by water more rapidly than ethyl sulphate (Claesson, A., 1879, 775; Kremann, A., 1907, ii, 241), but in the presence of potassium hydroxide the ratio of the reaction velocities is very different from that observed for the hydrolysis by water only. With $0.5N$-potassium hydroxide at 25°, the unimolecular constant for methyl sulphate is forty-five times as great as for the ethyl ester, whereas with water only the ratio is approximately 5:1. In order to decide whether the difference is due to the difference in the solubility of the two esters in water, and to avoid the possibility of such a disturbing factor, it is desirable to examine the rate of reaction in a homogeneous system. Kremann (A., 1907, ii, 157) has already observed that with methyl and ethyl alcohol, the rate of reaction of methyl sulphate is three to four times that of ethyl sulphate. With an alcoholic solution of sodium ethoxide, however, at 25° methyl sulphate reacts approximately twenty-five times as rapidly as ethyl sulphate, whilst at 0° the ratio is 58:1. The reaction in each case proceeds as far as the corresponding alkyl hydrogen sulphate or its sodium salt, any further hydrolysis being negligible. These results demonstrate that the great difference in the velocities of reaction of alkali on the two alkyl sulphates is not mainly due to any difference of solubility on the part of the sulphates, because a similar difference is observed in homogeneous and in heterogeneous systems. The difference is therefore presumably to be attributed to the different character of the reactions, the alkali hydrolysis yielding the alkali salt of the alkyl hydrogen sulphate, whilst the free alkyl hydrogen sulphate is produced by the action of water or of alcohol.

Examination of the reaction velocity of ethyl and methyl sulphates with alcohol in the presence of a gradually increasing proportion of water shows that the former ester is distinctly less soluble in water, and that the difference in the solubility of the two esters may exert an appreciable influence on the relative apparent reactivity of the two esters towards alkali hydroxide in the heterogeneous aqueous system. Methyl alcohol reacts with the two alkyl sulphates more rapidly than does ethyl alcohol, and although it was found that, as expected, sodium methoxide affects the methyl ester much more rapidly than the ethyl ester, the surprising result was obtained that sodium methoxide in methyl-alcoholic solution is less reactive than an ethyl-alcoholic solution of sodium ethoxide. A similar observation to this has already

been made in certain cases, for example, by Lobry de Bruyn and
Steger ·(A., 1899, i, 745, 849), Steger (A., 1889, i, 745), and
Kremann (A., 1905, ii, 307), but the suggestion of the last-named,
that the difference is due to the presence of traces of water
which cause a greater proportion of hydrolysis in the sodium
ethoxide, is discredited, and the suggestion is made that the ex-
planation may be found in the possible occurrence of the reaction
between the alkyl sulphate and the undissociated portion of the
sodium alkoxide (compare Wegscheider and Amann, A., 1915,
ii, 757). D. F. T.

The Velocity of Formation of Nitrosyl Bromide, $2NO + Br_2 = 2NOBr$. MAX TRAUTZ and VASANJI P. DALAL (*Zeitsch. anorg. Chem.*, 1918, **102**, 149—172. Compare A., 1916, ii, 304, and
this vol., ii, 151).—The investigation of this reaction was limited
to temperatures between $-15°$ and $+15°$, to bromine pressures
of 11—26 mm., and nitric oxide pressures of 11—12 mm. At
greater temperatures or pressures, nitrosyl bromide decomposes,
and at lower temperatures the bromine condenses on the glass of
the vessel. In presence of excess of bromine, the reaction appears
to be of the third order, the velocity constants found lying between
$0·9$ and $1·6 . 10^{10}$. Probably, however, there are two superimposed
reactions, the first, $NO + Br_2 \rightleftharpoons NOBr_2$, coming to equilibrium
very quickly, whilst the second, $NOBr_2 + NO \rightleftharpoons 2NOBr$, is
measurable. The temperature coefficient is very small, apparently
slightly greater than unity, and could not be determined with
certainty. On the supposition that the reaction takes place in the
above two stages, the "heat of activation" is calculated, and is
found to be 3076 cal. The velocity constants calculated from this
number agree substantially with the observed values and support
the authors' theory of thermochemical processes. E. H. R.

**Velocity of Dissolution of the Metals in Acids. III.
Velocity of Dissolution of Alloys of Zinc with Arsenic,
Lead, Cadmium, Nickel, Platinum, and Gold.** M. CENTNER-
SZWER (*Zeitsch. physikal. Chem.*, 1918, **92**, 563—580. Compare
A., 1914, ii, 550; 1915, ii, 158).—The observations previously made
on the rate at which hydrogen is evolved from solutions of hydro-
chloric acid by zinc–copper alloys have been extended to alloys of
zinc with other metals. The results obtained show that arsenic,
lead, and cadmium produce no increase in the rate of dissolution
of the zinc. The contrary observations recorded by previous
observers are attributed to the presence of traces of other metals—
probably iron or copper. The facts established by the author's
experiments are difficult to reconcile with the theory of local
elements.

Very small quantities of nickel, platinum, and gold of the order
of 0·01% produce an appreciable increase in the rate of dissolution
of zinc.

.The results obtained lead to the conclusion that pure zinc is

not acted on by either hydrochloric or sulphuric acid if the concentration is less than about 0·5 to 1N.   H. M. D.

Method for the Carrying Out of Catalytic Reactions.

JOHANN WALTER (D.R.-P., 295507; from *Chem. Zentr.*, 1917, i, 291).—Thorough exposure of the catalyst to the reagents is achieved by electromagnetic means. The catalyst itself may be magnetic and if desired spread on a non-magnetic material, or a non-magnetic catalyst may be deposited on a magnetic substance, and parts of the apparatus, such as baffle plates or gauze in a gas tube, or mechanical agitators, are made magnetic or magnetisable. During the reaction, or during the removal of the products, magnetic fields are established and broken by electrical means, so that the catalyst is kept moving, but near the exit of the apparatus a permanent field is maintained to prevent loss of the agent as dust. Examples given in the original specification include the hydrogenation of train oil, the preparation of methane from carbon monoxide, and the reduction of cinnamaldehyde to β-phenylpropaldehyde and β-phenylpropyl alcohol, lævulose to mannitol, and quinine to di- and tetra-hydroquinine.   J. C. W.

Some Problems of Atomic Stability.

J. W. NICHOLSON (*Proc. Physical Soc. London*, 1918, **30**, 65—82).—The author has investigated the dynamical stability of model atoms of pyramidal form consisting, for example, of a nucleus, a ring of electrons in the form of a circle the axis of which passes through the nucleus, and a single stationary electron on this axis. It is shown that no positively charged or neutral atom can exist in this form. Such structures are incompatible with a steady rotation of the ring electrons and cannot well form part of any molecular structure. The results appear to vitiate completely the molecular structures which have been formulated by Stark.   H. M. D.

Molecular Frequency and Molecular Number.

H. STANLEY ALLEN (*Phil. Mag.*, 1918, [vi], **35**, 338—349).—In a previous paper (compare this vol., ii, 14) it has been shown that the atomic number of an element is related to its characteristic frequency. Similar considerations have been applied to compounds, and it is shown that the formulæ $N\nu = n\nu_{A}$ and $N\nu = (n + \frac{1}{2})\nu_{A}$ represent the relations between the molecular number N and the characteristic frequency ν calculated from the specific heat at low temperatures or from Lindemann's formula. In these formulæ, n is an integer and ν_{A} the fundamental atomic frequency $= 21 \times 10^{12} (\text{sec.}^{-1})$.

The molecular number N of a compound $A_{a}B_{b}C_{c}$ is given by the equation $N = aN_{a} + bN_{b} + cN_{c}$, in which N_{a}, N_{b}, and N_{c} are the atomic numbers of the component elements. Evidence in support of the above formulæ connecting N and ν has been obtained by reference to the data for both inorganic and organic compounds. The agreement is such that the relations cannot be regarded as fortuitous.

It is suggested that the integer n (the frequency number) is related to the number of valency electrons which are concerned in imparting to the solid its crystalline structure.   H. M. D.

Glauber's Period in Amsterdam. W. P. JORISSEN (*Chem. Weekblad,* 1918, **15**, 268—271).—The register of the Western Church at Amsterdam records that "Johan Rudolph Glaubar" was interred on March 10th, 1670, proving the inaccuracy of the statement made by Goossen van Vreeswyck ("Silvere Rivier," The Hague, 1684, p. 117) that his death occurred on March 19th, 1670.   A. J. W.

Berend Coenders Van Helpen; a Groningen Alchemist of the Seventeenth Century. F. M. JAEGER (*Chem. Weekblad,* 1918, **15**, 285—302).—An account of the life, work, and family of the alchemist Berend Coenders van Helpen, a typical landed proprietor of the seventeenth century, who was born at Groningen in June, 1601, and died at Copenhagen on January 3rd, 1678.
A. J. W.

Willem Homberg. F. M. JAEGER (*Chem. Weekblad,* 1918, **15**, 316—337).—An account of the life and a list of the publications of Willem Homberg, who was born in Batavia on January 8th, 1652, and died in Paris on September 24th, 1715.   A. J. W.

Arrangement for Illuminating a Chemical Balance. B. D. PORRITT (*J. Soc. Chem. Ind.,* 1918, **37**, 85T).—A "tubolite" metallic filament lamp of 16 candle-power and 8·5 inches long is fitted on the top of the balance case; the lamp is enclosed in a semi-circular aluminium reflector, which serves to direct the light through the glass top of the case on to the beam and to screen the lamp from the eyes of the person using the balance.
W. P. S.

Inorganic Chemistry.

Production of Oxygen Free or almost Free from Chlorine. CHEMISCHE FABRIK GRÜNAU, LANDSHOFF & MEYER, EMIL FRANKE and FRIEDRICH SCHMIEDT (D.R.-P., 299505, 1915; from *Chem. Zentr.,* 1917, ii, 508).—By the addition of a small quantity of nickel or cobalt in the form of metal, oxide, or salt, the "first period" of development of oxygen from chlorates or perchlorates is prolonged; cerium dioxide also can be used as catalyst. The last traces of chlorine can be removed from the gas by passing this through a filter of magnesium oxide, whiting, or anhydrous sodium carbonate, which may be distributed over some inert material, such as glass wool or asbestos.   D. F. T.

Hydrogen Sulphide Generator. L. SATTLER (*J. Ind. and g. Chem.*, 1918, **10**, 226).—The main generator consists of a ge aspirator bottle the bottom tubulure of which is fitted with straight stop-cock connected with one of the tubulures of a ee-neck Woulfe bottle. Through the central orifice of the latter ube passes to the bottom of the bottle and is connected by a ber tube to an aspirator bottle placed at a higher level, which erns the pressure under which the apparatus works. The third fice of the Woulfe bottle serves for the passage of a siphon tube th stop-cock through which the waste acid can be discharged. e upper tubulure of the main generator carries a T-piece, one anch of which is connected with a tube dipping under mercury ming a safety-valve seal against excessive pressure. The other anch of the T-piece leads the generated gas through a stopck to a lead pipe terminating in a perforated coil submerged a washing bottle, through which the washed gas is delivered for e. The main generator is charged with about 23 kilos. of iron lphide and the high-level acid reservoir with about 14 litres of drochloric acid diluted 1:1 by volume. On opening the stopcks leading to and from the main generator, the three-neck ixing bottle should be filled with acid, and about 7·5 cm. of the id should remain in the reservoir.   J. F. B.

Synthesis of Ammonia at High Temperatures. EDWARD RADFORD MAXTED (T., 1918, **113**, 168—172).—From a rough lculation of the equilibrium between nitrogen, hydrogen, and nmonia, made by extending Haber's formulæ to temperatures bove 1000° abs., it appears that increase of temperature leads at rst to a rapid decrease in the proportion of ammonia until a inimum is reached, after which further increases cause the yield f ammonia to rise with increasing velocity. It should be possible, herefore, to realise a fair production of ammonia by heating ixtures of hydrogen and nitrogen to high temperatures and uddenly cooling the hot gases.

The subject has been examined experimentally by igniting mixures of nitrogen, hydrogen, and oxygen in a tube (*a*) under water, o that the hot gases were cooled by the water itself, or (*b*) cooled xternally by being made the tube of a Liebig's condenser. The lirect cooling (*a*) proved to be far more efficient, and with a mixure of gases in the proportions $N:H:O = 1:43:20$, giving a flame vith temperature 2580° abs., the yield of ammonia was as much s 1·23% at atmospheric pressures.

For experimental details, see the original.   J. C. W.

Preparation of Carbon Monoxide. BERTRAM BLOUNT (*Analyst*, 1918, **43**, 88).—Fairly pure carbon monoxide, free from carbon dioxide, may be obtained by heating a mixture of calcium oxalate and calcium oxide. The gas usually contains some sulphur dioxide if it is prepared from potassium ferrocyanide and sulphuric acid, or carbon dioxide if made from oxalic acid and sulphuric acid.   W. P. S.

Preparation of Argon in the Laboratory. MAX BODENSTEIN and LILI WACHENHEIM (*Ber.*, 1918, **51**, 265—270).—Samples of oxygen prepared from the air usually contain argon, occasionally as much as 3%. The commercial product can therefore be used as a source of argon, the oxygen being removed by combination with hydrogen. For this purpose, the authors have designed an apparatus, which is described and figured in the text. The control of the process requires a certain amount of manipulative skill, but even on the laboratory scale it only takes about two hours to prepare a litre of argon.

The hydrogen and oxygen, supplied from cylinders with good valves, are led into a small quartz combustion chamber through gas current manometers, the water is then trapped in two condensers, and the issuing gas made to pass through a sensitive gas current manometer. If this records minimum rate of flow, it indicates that neither oxygen nor hydrogen is being supplied in excess; if not, the gases are regulated accordingly. After this manometer are placed a hot tube containing copper oxide and copper to trap any traces of uncombined gases, then another condenser for the water, and finally an iron gas-washing tube containing calcium turnings heated electrically to 600°. This serves to absorb any nitrogen that may be present.

The process is based on a method described by the Griesheim-Elektron Co., D.R.-P., 295572 of 1913.　　　　J. C. W.

Production of Mono-, Di- and Tri-metallic Alkali Perphosphates and Perarsenates. S. ASCHKENASI (D.R.-P., 299300, 1914; from *Chem. Zentr.*, 1917, ii, 438).—By the addition of the necessary quantity of alkali to a solution of barium peroxide in aqueous arsenic or phosphoric acid, barium arsenate or phosphate is precipitated, and the filtrate containing the per-salt is then evaporated with slight warming and under reduced pressure; an aqueous solution of a mixture of sodium peroxide with the primary or secondary alkali salts can also be submitted to evaporation. If a solution of an arsenate, phosphate, or borate in dilute hydrogen peroxide is evaporated to dryness with gentle warming and under reduced pressure, the corresponding per-salt, for example, sodium perborate, can be obtained with scarcely any loss of oxygen.
　　　　　　　　　　　　　　　　　　　　　　D. F. T.

Influence of Calcium Sulphate on the Corrosive Action of Water on Iron. P. MEDINGER (*Ber.*, 1918, **51**, 270—271). —The fact that gas and water mains suffer corrosion particularly severely in heavy clays which contain calcium sulphate is explained as follows: through the ionisation of the sulphate, the proportion of calcium ions in solution becomes so great that the dissociation of the calcium hydrogen carbonate is depressed, and, consequently, the production of H and HCO_3 ions from the free carbonic acid is not so much hindered. The enhanced acidity of a solution containing free carbonic acid and calcium hydrogen carbonate con-

sequent on the addition of calcium sulphate may be demonstrated by means of litmus.   J. C. W.

Iron Trisulphide. WERNER MECKLENBURG and V. RODT (*Zeitsch. anorg. Chem.*, 1918, **102**, 130—148).—The work of previous investigators has left undecided the question of the existence of ferric sulphide. The authors have studied the action of hydrogen sulphide on ferric hydroxide, of alkali sulphides on ferric salts, and of alkali polysulphides on ferrous salts. When hydrogen sulphide is passed for a long time (about twelve hours) through an aqueous suspension of freshly prepared ferric hydroxide at the ordinary temperature in absence of air, the colour of the hydroxide gradually becomes black, and when the reaction is finished, the composition of the precipitate corresponds with Fe_2S_3, aq. The precipitate contains no sulphur soluble in carbon disulphide and is completely decomposed by dilute hydrochloric acid, forming ferrous chloride, hydrogen sulphide, and sulphur. Treatment with carbon disulphide, however, changes the character of the trisulphide, rendering it partly insoluble in dilute hydrochloric acid. The hydrated trisulphide is rapidly decomposed by air, and in absence of air it undergoes spontaneous decomposition into ferrous sulphide and iron disulphide. It can be completely dried in a vacuum over phosphoric oxide. The anhydrous trisulphide is pyrophoric if suddenly brought into contact with air, but if spontaneous ignition is prevented, it is quite stable.

By addition of a solution of a ferric salt to excess of sodium sulphide solution, a precipitate is produced having the composition $Fe_2S_3.Na_2S$, and the same compound is formed by the action of excess of sodium polysulphide solution on a solution of a ferrous salt. The alkali sulphoferrites form dilute aqueous colloidal solutions having a deep green colour.   E. H. R.

Reactions in Non-aqueous Solvents. II. The Action of Chromyl Chloride on Phosphorus Haloids. HARRY SHIPLEY FRY and JOSEPH L. DONNELLY (*J. Amer. Chem. Soc.*, 1918, **40**, 478—482).—The action of chromyl chloride on phosphorus di-iodide, tri-iodide, pentachloride, and pentabromide in anhydrous carbon tetrachloride has been examined.

With phosphorus di-iodide, a brown-coloured additive compound, CrO_2Cl_2,PI_2, is precipitated. It is readily decomposed by water with liberation of iodine and the formation of a solution containing phosphate, chromic, chloride, and iodide ions.

Phosphorus tri-iodide also yields an additive compound, CrO_2Cl_2,PI_3, which, when dry, consists of a purplish-red powder. It is decomposed by water in accordance with the equation $2CrO_2Cl_2,PI_3 + 4H_2O = 4HCl + 4HI + 2CrPO_4 + I_2$.

With phosphorus pentachloride, the additive compound CrO_2Cl_2,PCl_5 is produced in the form of a yellowish-red powder readily decomposed by water.

It has been previously found (A., 1916, ii, 626) that phosphorus

tribromide reacts according to the equation $2CrO_2Cl_2 + 3PBr_3 = 2CrOCl,POBr_3 + PBr_3Cl_2$, and the product obtained by interaction of chromyl chloride with phosphorus pentabromide appears to be a mixture of $CrOCl,POBr_3$ and the additive compound CrO_2Cl_2,PBr_5. The formation of these substances is presumably connected with the fact that phosphorus pentabromide is measurably dissociated into the tribromide in carbon tetrachloride solution. H. M. D.

The Reaction between Antimony and Solutions of Sodium in Liquid Ammonia. EDWARD B. PECK (*J. Amer. Chem. Soc.*, 1918, **40**, 335—347).—Metallic antimony dissolves when brought into contact with a solution of sodium in liquid ammonia. The atomic ratio of antimony to sodium in the saturated solution increases from about 1·2 for a solution containing 0·005 gram atom of sodium per litre to about 2·3 for a solution containing 0·4 gram atom of sodium per litre. For more concentrated solutions, the ratio diminishes slightly. The diminution may be due to the failure to reach equilibrium in the more concentrated solutions which are highly viscous, or it may possibly be accounted for by the fact that the solution was assumed to have the same volume as the ammonia which it contained.

The observed facts suggest that there are at least two compounds formed, in one of which the ratio Sb:Na is greater than two, whilst in the other this ratio is less than two.

The electrolytic behaviour of these solutions, when subjected to the action of a current between a platinum anode and an antimony cathode, has also been examined, but the quantitative data do not permit of any definite conclusion. The results show, however, that antimony is present in the solutions as anion, and that more than one atom of antimony is associated with each negative charge. H. M. D.

A New Metastable Form of Antimony Tri-iodide. A. C. VOURNASOS (*Compt. rend.*, 1918, **166**, 526—528).—Antimony tri-iodide, regarded as trimorphous, may be obtained in a fourth form by cooling a hot saturated solution of the red iodide in glycerol. It is thus obtained as an amorphous, yellow powder, m. p. 172°, at which temperature it steadily passes into the red variety, forming hexagonal crystals. This metastable, amorphous form may also be obtained from the red form by warming it on a water-bath with fifteen times its weight of acetic acid and a little potassium acetate. The solution on cooling deposits the yellow, amorphous iodide. It may also be prepared from antimony trioxide and potassium iodide by heating them at 100° with an excess of anhydrous acetic acid. The last method also applies to the preparation of arsenic, antimony, and bismuth tribromides, and arsenic and bismuth tri-iodides. W. G.

Mineralogical Chemistry.

The Gyrohedral Character of Rock Salt. R. GROSZ (*Centr. Min.*, 1918, 1—19).—The crystal structure deduced by W. H. and W. L. Bragg for sodium chloride and other similar salts is stated not to be satisfactory. On the one hand it is a holohedral structure, whilst there is abundant evidence that the structure of sylvine is gyrohedral hemihedral, and that other salts of the same series are certainly not holohedral; on the other hand, no account is taken of the chemical bonds between individual atoms. By symmetrically displacing the centres of gravity of selected atoms in the Bragg structure, a number of new structures can be produced having gyrohedral or tetartohedral symmetry, and it is claimed that these cannot be distinguished by X-ray analysis from the holohedral form. If rock salt were tetartohedral, irregularities might be expected to appear in the Laue radiogram, but such irregularities the author has failed to discover.

It has been shown by Smits and Scheffer (A., 1917, ii, 78) that it is possible to couple symmetrically the atomic valencies in a cubic structure of atoms of two kinds. The coupling leads to the formation of cubic aggregates of different sizes according to the disposition of the planes of atoms, and these aggregates may be regarded as crystal molecules. The structure derived by the association of such aggregates affords an explanation of the cubic cleavage of rock salt, since at regular intervals there occur in the series of {100} planes pairs of planes between which no chemical bonds are active. A crystal cleaved along these planes of zero affinity would contain no excess of uncombined atoms of either kind, whereas in other crystal models the "ideal" crystal always contains an excess of atoms of one kind.

The hemihedral character of the crystals of rock salt may also be accounted for by making certain assumptions regarding the axis and direction of rotation of the valence electrons about the individual atoms.   E. H. R.

Algodonite and Whitneyite. L. H. BORGSTRÖM (*Geol. För. Förh.*, 1916, **38**, 95—100; from *Jahrb. Min.*, 1918, Ref. 11—13). —Analyses of algodonite and whitneyite from the Mohawk mine, Michigan, gave Cu 84·1 and 87·2% respectively. Melting-point determinations in capillary tubes showed a wide interval, sintering beginning at 695°, but fusion was complete only at 100° higher. These minerals are therefore decomposed before fusion takes place. The cooling curves of the fused materials show in each case a pronounced break at 688°, that is, near the freezing point (685°) of the eutectic Cu_3As—Cu. Polished plates of the natural minerals and of the fused products were etched with nitric acid and examined under the microscope. Algodonite was seen to consist of almost homogeneous crystalline material with very little metallic

copper, whilst whitneyite contains 3—4% of metallic copper, and thus consists of a mixture of algodonite and copper. The fused products in each case consist of a mixture of light grey Cu_3As and copper. The electrical resistance in ohms for rods 1000 mm. long and 1 sq. mm. cross-section is for whitneyite 0·341 and 0·335, for algodonite 0·415, and for the fused materials 0·469 and 0·634 respectively. Although not indicated on the cooling diagrams of copper-arsenic fusions, the copper arsenide, Cu_6As (algodonite), therefore exists, but is only stable below the point of fusion. On the other hand, the arsenide Cu_9As (whitneyite) has no existence.

L. J. S.

Spectral Investigation of the Composition of Goyazite. A. DE GRAMONT (*Bull. Soc. franç. Min.*, **40**, 26; from *Chem. Zentr.*, 1917, ii, 825).—According to spectral observations, calcium, strontium, and probably aluminium are characteristic constituents of goyazite.

H. M. D.

Meerschaum from Kraubat, Styria. H. LEITMAIER (*Sitzungsber. K. Akad. Wiss. Wien, Math.-Nat. Kl.*, Abt. I, 1915, **124**, 163—180; from *Jahrb. Min.*, 1918, Ref. 21—22).—The meerschaum occurs as bands 1 mm. to 20 dcm. thick in massive magnesite. It is white, yellow, or green, and either earthy (being then mixed with magnesite), or compact with large-conchoidal fracture. Analysis of the latter variety gives the formula $2MgO,3SiO_2,4H_2O$. About half of this water is lost over sulphuric acid at 20°, and is reabsorbed from a moist atmosphere to the extent of 37·56% H_2O after 144 hours. At 100° the loss is 9·72%, and at 450° it is 18·17%. Since $2H_2O$ is more closely held, the formula is written $2MgO,3SiO_2,2H_2O$, any extra water present depending on the vapour tension of the surrounding atmosphere. The meerschaum and magnesite have probably originated by the action of carbonated waters on serpentine. When fused, the meerschaum gives rise to an enstatite containing an excess of silica $(MgO : SiO_2 = 7 : 9)$, which is probably held in solid solution.

L. J. S.

The Identity of Shattuckite and Plancheite. F. ZAMBONINI (*Compt. rend.*, 1918, **166**, 495—497).—The mineral shattuckite as described by Schaller (*J. Washington Acad. Sci.*, 1915, **5**, 7) and the mineral plancheite as described by Lacroix (A., 1908, ii, 508) possess the same optical and crystallographic properties, although differing slightly in their chemical analyses. As a result of the examination of a specimen of plancheite, the author has obtained analytical data in agreement with those for shattuckite and for the composition $2CuSiO_3,H_2O$, and he considers that these two minerals are identical and that the older name plancheite should be retained.

W. G.

Gedrite from the Tatra Mountains, Hungary. W. PAWLICA (*Bull. Acad. Sci. Cracow, Cl. Sc. Math. et Nat.*, Ser. A, 1915, 18—25; from *Jahrb. Min.*, 1918, Ref. 19—20).—Analysis I is of a

gedrite-gneiss from the Gewont peak, containing quartz (41·3 mol. %), plagioclase (a basic oligoclase, $Ab_{72}An_{28}$, 35·3), gedrite (13·0), biotite (5·1), ilmenite (1·3). The gedrite (anal. II, mean of three) forms black, orthorhombic prisms ½—3 cm. long and 0·1 mm. thick with distinct pleochroism, bluish-green to pale green. The high percentage of fluorine and water is not accounted for by the ordinary formula, but in Penfield's amphibole formula it figures in the molecule, $(F,HO)_2Mg(Al,Fe''')SiO_5$, which is here present to the extent of 39·6%, with the metasilicate molecules, $MgSiO_3$ (26·6), $FeSiO_3$ (25·7), $CaSiO_3$ (7·2), and Na_2SiO_3 (0·9%).

	SiO_2.	TiO_2.	P_2O_5.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.
I.	69·82	1·24	0·18	12·70	2·32	2·78	0·12	2·96	2·47
II.	41·59	0·97	0·16	12·81	5·90	14·81	trace	3·55	15·13

	K_2O.	Na_2O.	F.	H_2O <105°.	H_2O >105°.	Total less O for F.	Sp. gr.
I.	0·40	3·27	0·17	0·23	1·30	99·89	3·240
II.	0·12	0·43	2·34	0·86	1·68	99·42	2·701

L. J. S.

Iron Silicate Ores of the Diabase and Schalstein Zone tween Sternberg (Moravia) and Bennisch (Austrian lesia). FRANZ KRETSCHMER (*Jahrb. Min.*, 1918, 19—42).—A tailed account is given of the characters of these ores as seen in cro-sections, an account of their chemical characters having en sent for publication in *Arch. Lagerstättenforsch., Berlin.* e dense, chloritic minerals of which these ores are composed clude thuringite and moravite (A., 1906, ii, 458), and two new ecies, viridite and mackensite, differing from the former in coning more iron (respectively ferrous and ferric), and correspondgly less alumina. *Viridite* contains only 4·49% Al_2O_3, and approxates to the end-member $4FeO,2SiO_2,3H_2O$. It is a compact, leeken ore, D 2·89, H 3—3½, and under the microscope is seen to nsist of minute needles and scales with pearly, micaceous cleavage. *ackensite* contains 6·14% Al_2O_3 (in part due to the presence of imixed thuringite), and approximates to the end-member, $e_2O_3,SiO_2,2H_2O$, of the thuringite series. It is compact, ironlack to greenish-black, D 4·89, H 3—3½, and under the microope shows colourless or brownish-green needles surrounding shreds thuringite and grains of calcite and magnetite. Locally, the agnetite is present in greater relative amount, but ores of this haracter are not abundant. L. J. S.

Analytical Chemistry.

Increasing the Delicacy of Delivery of Burettes. EWART L. MERRITT (*Analyst*, 1918, **43**, 138).—Both the inside and the utside of the jet of the burette are coated with a thin film of

paraffin (m. p. about 55°); the number of drops per c.c. delivered
by the burette may be thus increased from twenty to forty.

W. P. S.

A New Process of Quantitative Analysis. ALBERTO BETIM
PAES LEME (*Compt. rend.*, 1918, **166**, 465—467).—The method is
a spectrographic one, using a screen having a narrow, horizontal
opening and travelling with a constant velocity in a vertical direc-
tion during the vaporisation of a known weight of the mineral
containing the element to be estimated. The width of the open-
ing and the velocity of the screen are equal. A given ray for the
element is adopted once and for all, and the time during which it
is visible is determined. An example is given, aluminium being
the metal to be estimated.

W. G.

Detection of Small Quantities of Chlorine in Iodine.
J. PINKHOF (*Pharm. Weekblad*, 1918, **55**, 236).—The presence of
chlorine in iodine between $\frac{1}{8}$% and 2% can be detected by neutral-
isation with thiosulphate and precipitation with barium nitrate
of the sulphate formed.

A. J. W.

Estimation of Chlorides in Blood. MARCEL DUGARDIN
(*Ann. Chim. anal.*, 1918, **23**, 59).—Ten c.c. of the serum are
mixed with 10 c.c. of 20% trichloroacetic acid solution, the mixture
is filtered, and 10 c.c. of the filtrate are diluted with 25 c.c. of
water, then acidified with 5 c.c. of nitric acid, and the chloride is
titrated by Volhard's method.

W. P. S.

[Estimation of Sulphur in Ores, etc.] F. G. HAWLEY
(*Eng. and Min. J.*, 1918, **105**, 385—386).—A method is described
for estimating sulphur gravimetrically in ores and furnace product
by oxidation to sulphate and precipitation as barium sulphate,
which avoids the difficulties usually experienced in oxidising matte
and calcines, or ores containing much copper or zinc sulphide.
The oxidising mixture employed is a 20% solution of sodium
chlorate to which is added a small quantity of a mixture of equal
parts of bromine and glacial acetic acid, followed by an equal
volume of nitric acid nearly saturated with potassium chlorate.
[For details, see *Ind.*, May.]

W. F. F.

Some Limitations of the Kjeldahl Method. HARVEY C.
BRILL and FRANCISCO AGCAOILI (*Philippine J. Sci.*, 1917, **12**,
261—265).—The Kjeldahl method yields low results when applied
to the estimation of nitrogen in pyridine, piperidine, quinoline,
*iso*quinoline, hydroxyquinoline, pyrrole, and sometimes in nicotine;
this is possibly due to the formation of sulphonic derivatives, which
resist decomposition. In the case of pyridine, the Gunning-Arnold
method gives trustworthy results if the heating is prolonged for a
considerable period (four hours) after the solution has become
clear. Low results are always obtained when sodium sulphate is
used in place of potassium sulphate for raising the boiling point
of the mixture. [See, further, *Ind.*, 225A.]

W. P. S.

Kjeldahl's Method for the Estimation of Nitrogen.
EDUARD SALM and SIEGFRIED PRAGER (*Chem. Zeit.*, 1918, **42**, 104—105).—The addition of zinc dust is necessary in the distillation of the ammonia obtained by digesting a nitrogenous substance with sulphuric acid and mercury or with sulphuric acid, phosphoric oxide, and mercury, if potassium sulphide is not added to the sodium hydroxide. If potassium sulphide is used, zinc turnings may be used in place of zinc dust. The results obtained are too low if the zinc is omitted or replaced by aluminium. [See, further, *Ind.*, May.] W. P. S.

Foam Inhibitor in the Van Slyke Amino-nitrogen Method.
H. H. MITCHELL and H. C. ECKSTEIN (*J. Biol. Chem.*, 1918, **33**, 373—375).—The formation of foam during the liberation of nitrogen in the Van Slyke apparatus is prevented by the addition of two or more drops of diphenyl ether, which is readily synthesised from bromobenzene and potassium phenoxide (Ullmann and Sponagel, A., 1905, i, 644). H. W. B.

Alkalimetric Estimation of Phosphorus in Iron and Steel.
KOLAUS CZAKO (*Chem. Zeit.*, 1918, **42**, 53—54).—When the slow ammonium phosphomolybdate precipitate is dissolved in a known excess of sodium hydroxide solution and the excess then titrated with standardised nitric acid, it is recommended that the latter be standardised against potassium hydrogen carbonate. The potassium hydrogen carbonate value of the acid is then multiplied 0·013481 to obtain the phosphorus value. W. P. S.

Separation of Phosphorus from Vanadium. ALFRED ROPF (*Chem. Zeit.*, 1917, **41**, 877—878, 890—891).—One gram of the alloy containing phosphorus and vanadium is dissolved in aqua regia, the solution evaporated to dryness, the residue heated gently, then cooled, boiled with the addition of 20 c.c. of hydrochloric acid (D 1·12), diluted to 60 c.c., and filtered to separate silica. The filtrate is treated with 15 c.c. of ammonium citrate solution prepared by neutralising 1 kilo. of citric acid with ammonia and diluting the solution to 5 litres), and boiled for three minutes to reduce the vanadic acid; after the addition of 30 c.c. of 40% ammonium nitrate solution and 10 c.c. of nitric acid (D 1·18), the phosphoric acid is precipitated with molybdic acid reagent. In the case of ores, the sample is fused with a mixture of sodium and potassium carbonates, or sodium carbonate and potassium nitrate, the mass dissolved in water, filtered, and the filtrate treated as described. If arsenic is present, it may be separated from the vanadium and phosphorus by treatment with hydrogen sulphide, or the phosphorus, together with some of the vanadium, may be precipitated as hydrated aluminium phosphate, and thus separated from the arsenic. W. P. S.

Spectroscopic Detection of Boron. A. DE GRAMONT (*Compt. rend.*, 1918, **166**, 477—480).—Boron may be readily detected if

present to the extent of 1 in 10,000 by means of the ray λ 3451·2 and the doublets λ 2497·82 and 2496·87, shown in the condensed spark spectrum.   W. G.

Gasometric Estimation of combined Carbon Dioxide.

W. MESTREZAT (*Ann. Chim. anal.*, 1918, **23**, 45—47).—A method for the estimation of carbon dioxide in a mixture containing a carbonate and a hypochlorite consists in treating a portion of the sample with sulphuric acid and measuring the volume of the liberated carbon dioxide after the chlorine has been absorbed by oil of turpentine. The estimation is carried out in an ordinary calcimeter, but a tube containing a plug of cotton wool impregnated with oil of turpentine is placed between the reaction flask and the gas-measuring burette. ' [See, further, *Ind.*, May.]   W. P. S.

Estimation of Potassium.

BERTRAM BLOUNT (*Analyst*, 1918, **43**, 117—120).—For the estimation of potassium in siliceous rocks, clays, etc., the material is decomposed with hydrofluoric and sulphuric acids, iron, aluminium, manganese, and calcium are removed from the solution in the usual way, sulphuric acid is separated by treatment with barium hydroxide, and the solution is evaporated to obtain the mixed sodium and potassium chlorides. The quantity of potassium is then estimated by the platinum chloride or perchlorate method.
                                                         W. P. S.

Calcium in Man. I. Estimation of Calcium in the Blood.

W. H. JANSEN (*Zeitsch. physiol. Chem.*, 1918, **101**, 176—192).—The blood (10 c.c.) is dried and incinerated. The ash is dissolved in hydrochloric acid, nearly neutralised with ammonia, and the iron and phosphorus removed by boiling with ammonium acetate. The calcium is subsequently precipitated as oxalate from the carefully neutralised filtrate. The precipitate is collected, and, after ignition in the usual way, the residual calcium oxide is estimated by dissolving in a known volume of $N/100$-hydrochloric acid and titrating the excess with alkali or by dissolving in 15 c.c. of $N/100$-hydrochloric acid, adding 25 c.c. of water, 2 c.c. of a 10% potassium iodide solution, 4 drops of a 4% potassium iodate solution, and 2 drops of a 1% starch solution in 20% potassium chloride solution, and then titrating with $N/100$-thiosulphate solution until the blue colour just disappears.   H. W. B.

Estimation of Hardness of Water by the Method of Wartha-Pfeiffer.

WAGNER (*Zeitsch. öffentl. Chem.*, 1917, **23**, 375—379. Compare A., 1914, ii. 490).—This method yields more trustworthy results, particularly in the case of waters containing relatively large quantities of magnesium salts, if the amounts of sodium carbonate and sodium hydroxide in the reagent are increased to 14·5 grams and 8·01 grams per litre, respectively.
                                                         W. P. S.

Estimation of Sulphur and Copper Oxide. C. G. MAIER (*Eng. and Min. J.*, 1918, **105**, 372—373).—For estimating the proportions of copper sulphide and "oxide" or soluble copper in a sample of copper ore, especially for use in flotation processes, the ore is heated with 4% sulphuric acid at 80—90°, the mixture cooled, and clean mercury added and mixed thoroughly with the residue so that it amalgamates with the metallic copper present or reduced from cuprous oxide. The solution is filtered, and the copper determined separately in the filtrate and residue, preferably by the iodide method. The copper in the residue represents the sulphide and that in the solution the "oxide" or soluble copper. [See, further, *Ind.*, May.] W. F. F.

Copper Dicyanodiamide and its Use in Analysis. H. GROSS-MANN and J. MANNHEIM (*Chem. Zeit.*, 1918, **42**, 17—19).—Copper may be precipitated by treating a solution of one of its salts with concentrated dicyanodiamide sulphate solution, rendering the mixture slightly ammoniacal, heating it to boiling, and then adding sodium hydroxide solution until the blue colour changes to reddish-violet. After cooling, the red precipitate is collected, washed with cold water, and dried at 120°; it contains 23·92% of copper. As the precipitate is slightly soluble in water, all the solution used should be concentrated. Nickel may be precipitated in a similar way (compare A., 1907, ii, 819), and the method may be used for the separation of copper and nickel from zinc, aluminium, chromium, arsenic, lead, and antimony. In exceptional cases, where the introduction of alkali into the solution is not desired, dimethylamine may be used in place of sodium hydroxide to precipitate the copper and nickel compounds. W. P. S.

Analysis of Aluminium Alloys. BERNARD COLLITT and WILLIAM REGAN (*J. Soc. Chem. Ind.*, 1918, **37**, 91—94T).—Methods are given for the estimation of copper, iron, nickel, manganese, zinc, magnesium, and silicon in aluminium alloys such as are used in the construction of aircraft and other engines of warfare. In cases where the alloy contains only copper (10 to 15%) and manganese (1%) in addition to aluminium, the copper may be estimated volumetrically by the iodide method; in other alloys it is estimated gravimetrically by precipitation as sulphide by thiosulphate, the sulphide being subsequently ignited and weighed as oxide. The original should be consulted for the details of the methods recommended for the estimation of the other constituents. W. P. S.

Volumetric Estimation of Manganese by means of Sodium Arsenite. FRED IBBOTSON (*Chem. News*, 1918, **117**, 157—158).—When permanganate solution containing nitric acid is titrated with sodium arsenite solution, the latter has a reducing value about 33% in excess of the value it has when used against potassium permanganate solution alone. This appears to be due to the formation of manganic compounds in the presence of nitric acid. [See, further, *Ind.*, May.] W. P. S.

Estimation of Manganese in Aluminium Alloys and Dust.
J. E. CLENNELL (*Eng. and Min. J.*, 1918, **105**, 407—410).—Two
methods are described for estimating manganese in dust made from
aluminium–manganese alloys.   Several known methods were in-
vestigated, but the following much simpler methods are preferred:
1 Gram of the sample is carefully heated with 50 c.c. of 50% nitric
acid, and finally boiled to expel oxides of nitrogen.   The solution
is filtered, the residue washed, placed in a nickel crucible, dried,
ignited, and the ash covered with sodium peroxide.   The mixture
is fused, and the product dissolved in water and added to the
previous nitric acid solution.   The mixture is boiled, and about
1 c.c. of standard silver nitrate solution added to remove chlorides.
0·1 Gram of lead peroxide is added for each estimated 0·1 gram
of manganese present, the mixture boiled, cooled, made up to
100 c.c., and filtered.   Fifty c.c. of the filtrate are titrated with
standard sodium arsenite which has been standardised against a
manganese salt.   Another method is described in which ammonium
persulphate is substituted for lead peroxide, but this was not so
trustworthy owing to the variability in the quality of the per-
sulphate. [For details, see *Ind.*, May.]   W. F. F.

Gravimetric Estimation of Chromates and Dichromates.
L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, 46—48).—
I. *As Barium Chromate.*—One hundred c.c. of a neutral solution
containing about 0·2% of an alkali chromate are treated with 1 c.c.
of $N/10$-acetic acid and 1 gram of sodium chloride, heated to boil-
ing, and 5 c.c. of 10% barium chloride are added slowly while the
mixture is stirred.   The mixture is kept boiling for three minutes,
then cooled, and, after eighteen hours, the precipitate is collected,
washed with 50 c.c. of cold water, dried at 132°, and weighed.
When the precipitate weighs less than 0·1 gram, the weight found
is about 1 mg. too low.   If the precipitate is ignited before being
weighed, it loses 0·25% in weight.   The presence of ammonium,
potassium, magnesium, and calcium chlorides does not interfere,
but nitrates, chlorates, and acetates cause the results to be too
high.   Dichromates are estimated in a similar way after their solu-
tion has been boiled with the addition of calcium carbonate and
filtered.   II. *As Silver Chromate.*—This method must be used if
the chromate solution contains sulphate; in any case, it is more
trustworthy than the barium chromate method, but cannot be used
in the presence of chlorides.   One hundred c.c. of the chromate
solution (or dichromate solution after treatment with calcium
carbonate) are boiled and 5 c.c. of 10% silver nitrate solution are
added.   After eighteen hours, the precipitate is collected, washed
with 50 c.c. of water saturated previously with silver chromate,
dried at 132°, and weighed.   The results are not affected by the
presence of nitrates, chlorates, or acetates, but sulphates cause the
results to be too high.   W. P. S.

Colorimetric Estimation of Tungsten. A. TRAVERS (*Compt.
rend.*, 1918, **166**, 416).—For this method, using titanous chloride

(compare A., 1917, ii, 545), the tungsten solution should not contain more than 0·1 gram of the metal in 100 c.c., and the acidity of the solution should not exceed $N/10$. The estimation cannot be performed in the presence of vanadium, phosphorus, or molybdenum. W. G.

[**Estimation of Uranous Salts in Presence of Formic Acid.**] E. C. HATT (*Zeitsch. physikal. Chem.*, 1918, **92**, 513—562).—Compare this vol., ii, 144.

Oxidimetric Estimation of Thorium Precipitated as the Oxalate. F. A. GOOCH and MATSUSUKE KOBAYASHI (*Amer. J. Sci.*, 1918, [iv], **45**, 227—230).—The following conditions are given for the estimation of thorium by titration, with permanganate, of its oxalate, or of the excess of oxalic acid used for the precipitation. The oxalate is precipitated by adding the thorium solution to an excess of cold oxalic acid solution; the reverse procedure is less trustworthy owing to the formation of basic compounds, especially in hot solutions. After thirty minutes, the precipitate is collected on an asbestos filter, washed with cold water containing one drop of concentrated sulphuric acid in each 25 c.c., the filter and precipitate are then transferred to a beaker containing 100 c.c. of water, the mixture is heated at 85°, 5 c.c. of sulphuric acid (1:1) are added, and the solution is titrated with $N/10$-permanganate solution until the greater part of the oxalate has been oxidised; the solution is then heated again at 85° and the titration completed. If a known excess of oxalic acid has been used, the filtrate from the oxalate precipitate may be heated at 85°. acidified with sulphuric acid, and titrated with permanganate. In this case, there is no need to reheat the titration mixture. The precipitated thorium oxalate has the composition $Th(C_2O_4)_2$. W. P. S.

The Estimation of Tantalum in its Alloys with Iron. A. TRAVERS (*Compt. rend.*, 1918, **166**, 494—495).—In the estimation of tantalum, the precipitate of tantalic acid usually contains some silica, and if this is removed by means of hydrofluoric acid, some of the tantalic acid is also lost. The tantalic acid may, however, be volatilised in a current of hydrogen chloride at 900°. The silica which is left is weighed, and the weight deducted from that of the original precipitate.

For details of application to steels, etc., see *Ind.*, 244A.

W. G.

Detection and Estimation of Methyl Alcohol, its Presence in Various Foodstuffs, and the Behaviour of Foodstuffs containing Methyl Alcohol in the Organism. TH. VON FELLENBERG (*Biochem. Zeitsch.*, 1918, **85**, 45—117. Compare A., 1917, i, 616).—A detailed account is given of the modification of Denigès's method for estimating methyl alcohol. The essential process consists in the oxidation of the liquid (which generally con-

tains ethyl alcohol) with permanganate, and the colorimetric estimation of the formaldehyde thus obtained by oxidation under standard conditions by magenta-sulphurous acid solutions.

A new method is also given for determining the presence of methyl alcohol when it is only present in small quantities. The essential process consists in the fractional separation of the mixed methyl and ethyl alcohols by potassium carbonate. The alcohol separated first by incomplete saturation with the carbonate contains scarcely any methyl alcohol. After separation of fractions containing only minute amounts of methyl alcohol, the residue is distilled. The distillate is fractionated, and the first fractions are redistilled. These fractions are again redistilled, the earlier fractions only being retained. A fraction is finally obtained which is rich in methyl alcohol, and this, after drying over calcium oxide, is converted into iodides, from which a fraction rich in methyl iodide can be separated.

It is shown that the methyl alcohol in certain spirits is derived chiefly from the pectin substances, from which 10—11% of methyl alcohol can be separated by treating with dilute sodium hydroxide.

The lignins of wood also yield methyl alcohol, but this is not eliminated so readily as that of pectins. It can be obtained in various fractions by treating the wood first with sodium hydroxide to eliminate the pectin alcohol, and then with graded strengths of sulphuric acid. Each filtrate obtained in this way is then treated with 70% sulphuric acid, and the methyl alcohol in the distillate is estimated, as well as the methyl alcohol in the distillate, before treatment with the 70% acid.

The methyl alcohol of the pectins and lignins was determined in a large number of different kinds of woods, etc.

An investigation was also made of the effect of ingestion of substances containing pectins. The ingestion of pectin-containing substances caused a small increase in the excretion of methyl alcohol in the urine, which was much more marked when ethyl alcohol was ingested at the same time. It was suggested that certain symptoms found in the drinkers of spirits may be due to the methyl alcohol contained therein. [See also *Ind.*, May.]   S. B. S.

Estimation of Glycerol by Wagenaar's Method. J. H. M. BECKERS and I. M. KOLTHOFF (*Pharm. Weekblad*, 1918, 55, 272—281).—Wagenaar's method of estimating glycerol (A., 1911, ii, 663) gives results dependent on the composition and temperature of the liquid. Methyl alcohol is without influence on the reaction, but the presence of ethyl alcohol, haloids, nitrates, and to a less degree sulphates, is deleterious. With fats, it is best to saponify with methyl-alcoholic potash and remove the fatty acids with the minimum quantity of sulphuric acid.   A. J. W.

Estimation of the Amount of Water in Glycerol. I. M. KOLTHOFF (*Pharm. Weekblad*, 1918, 55, 304—307).—An account of a method of estimating the percentage of water in glycerol by observing the temperature range of complete miscibility of mixtures

of the sample and aniline. A table showing the corresponding percentages of water is given. A. J. W.

Methylene-blue a Sensitive Reagent for the Detection of Picric Acid in Urine. ROZIER (*Bull. Sci. Pharmacol.*, 1917; from *Ann. Chim. anal.*, 1918, **23**, 63).—The urine is treated with normal lead acetate and filtered; 4 c.c. of the filtrate are placed in a test-tube, one drop of 0·5% methylene-blue solution is added, and the mixture is shaken with 1 c.c. of chloroform. After separation, the chloroform layer has a green colour if picric acid or picramic acid is present in the urine; in their absence, the chloroform is coloured blue. The test will detect the presence of 2 mg. of picric acid per litre of urine. W. P. S.

Colorimetric Estimation of Picric Acid and its Derivatives in Body Fluids. X. LAPORTE (*Bull. Soc. Pharm. Bordeaux*, 1917, No. 3; from *Ann. Chim. anal.*, 1918, **23**, 64).—A definite volume of the fluid (which should be diluted or concentrated so that it contains about 0·01 gram of picric acid per litre) is neutralised and treated with 0·5 c.c. of ferrous sulphate–tartaric acid reagent (compare A., 1917, ii, 158) and 1·5 c.c. of ammonia; these quantities of reagents are required for each 10 c.c. of the sample. The coloration obtained is compared with that produced by a known amount of picric acid under the same conditions. W. P. S.

Estimation of Cholesterol. I. LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1918, **101**, 89—98).—The author finds that the method described by Windaus (A., 1909, i, 172) for recovering the cholesterol or similar component from the digitonin–cholesterol complex is unsatisfactory. By the following procedure, a quantitative separation is effected. About 0·5 gram of the anhydrous complex is weighed out and boiled with 5 c.c. of acetic anhydride for twenty to thirty minutes under a reflux condenser. The hot liquid is poured into about 80 c.c. of water. After the product of the reaction has solidified, it is collected, washed, and dried in a vacuum. It is now removed as completely as possible from the filter paper, transferred to a small flask, dissolved in 10 c.c. of 90% alcohol, and mixed with 10 c.c. of 1% aqueous sodium hydroxide. The resulting emulsion is boiled for two and a-half to three minutes, cooled, diluted with water, acidified, and extracted with ether. The cholesteryl acetate dissolves in the ether, whilst the digitonin remains in the dilute alcohol. After evaporation of the ether, the cholesteryl acetate is hydrolysed with alcoholic potassium hydroxide, and the free cholesterol or similar compound extracted by ether, weighed, and subsequently identified in the usual way. H. W. B.

Detection of Acetone in Urine. HANS TRUNKEL (*Pharm. Zeit.*, 1918, **63**, 104—105)—Legal's nitroprusside test is trustworthy and gives the best results when applied as a ring test. Two

c.c. of the urine are mixed with ten drops of 20% sodium nitro-prusside solution and 1 c.c. of acetic acid, and 2 c.c. of ammonia are poured on the surface of the mixture; if acetone is present, a violet-red zone appears at the junction of the two liquids. Reichardt's test (A., 1916, ii, 119), in which the acetic acid of the Legal test is replaced by ammonium chloride, is less trustworthy, since a feeble coloration is obtained in the absence of acetone. It is not necessary for the nitroprusside solution employed to be freshly prepared; the solution, if made with the pure salt, keeps almost indefinitely.   W. P. S.

Estimation of Pyridine Bases in Ammonia and its Salts. T. F. HARVEY and C. F. SPARKS (*J. Soc. Chem. Ind.*, 1918, **37**, 41—43T).—The pyridine is precipitated as periodide from a sulphuric acid solution of the sample (ammonia, ammonium carbonate, or other salt) in the presence of sodium chloride, the periodide is converted into sulphate, and the latter titrated with alkali solution. When sufficient sodium chloride is added, 1 mg. of pyridine in 200 c.c. of $N/2$-sulphuric acid is precipitated completely as periodide. The method in detail is as follows: Fifty c.c. of the sample of ammonia (D about 0·885) is treated, in a separating funnel provided with a plug of cotton wool above the tap, with 100 c.c. of 10N-sulphuric acid, the mixture being cooled during the addition of the acid. Fifty grams of sodium chloride are then dissolved in the mixture, and 10 c.c. of iodine solution (iodine, 13 grams, and potassium iodide, 13 grams, per 100 c.c.) are added. The mixture is shaken, and, after fifteen minutes, the liquid portion is forced through the cotton wool filter; the precipitate is washed with 20 c.c. of a mixture of 10N-sulphuric acid, 10 c.c., water, 190 c.c., and iodine solution (see above), 10 c.c., then decomposed by a slight excess of saturated thiosulphate solution, diluted to about 20 c.c., and neutralised with $N/1$-sodium hydroxide solution, using methyl-orange as indicator. Phenolphthalein is then added, and the pyridine sulphate titrated with $N/10$-sodium hydroxide solution; 1 c.c. of the latter is equivalent to 0·0079 gram of pyridine. The solution employed for washing the periodide precipitate should be made about eighteen hours before using and be filtered if necessary.   W. P. S.

Colour Reactions in the Chemico-legal Examination of Bloodstains. LUCIANO P. J. PALET and AMANCIO FERNANDEZ (*Anal. Soc. Quim. Argentina*, 1917, **5**, 177—184).—A review of the various colour tests proposed for the identification of bloodstains.   A. J. W.